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INDUSTRIAL AND ENGINEERING CHEMISTRY

HARRISON E. HOWE, EDITOR

Solvent Refining of Lubricating Oils with Nitrobenzene

Analytical Methods

S. S. KURTZ, JR., C. E. HEADINGTON, AND B. ZIEBER, The Atlantic Refining Co., Philadelphia Pa.

THIS paper describes the analytical methods which have been worked out during the period covering the development of the operation and equipment for the nitrobenzene process for solvent refining of lubricating oils as described in previous papers (3, 4, 5). These methods are also useful in the control of the commercial plants now using this process. The discussion is divided into five parts: source of samples, analysis of nitrobenzene-oil solutions of low nitrobenzene content, analysis of nitrobenzene-oil solutions of high nitrobenzene content, analysis of nitrobenzene-water solutions, and analysis of charge stocks. Methods for determining the purity of fresh nitrobenzene can usually be supplied by the producers of this material.

Source of Samples

Table I gives a summary of the plant samples on which analyses might be desirable, the point from which the samples are taken as shown on the flow diagram in Figure 1, frequency of sampling, probable concentration, method used for the analysis, and the approximate time required for the analysis.

The water samples, instead of being taken from the line at *L*, are actually taken from the bottoms of a small still

The analytical methods presented can be used to determine the composition of the solvent-oil solution present in any part of the extraction system. Methods are also described for determining the concentration of low-boiling fractions in the charge oil and the concentration of nitrobenzene in water.

inserted at this point and used to recover the small amount of nitrobenzene dissolved in the water from a water separator. These units also receive the condensed steam from the vacuum pumps.

Because of the widespread differences in the nitrobenzene content of samples taken at different points in the plant, it

was necessary to develop several analytical methods giving the desired accuracy with a minimum expenditure of time. Accordingly, four groups of methods are presented: (1) methods for determining 0 to 5 weight-per cent of nitrobenzene in oil, (2) 5 to 100 weight-per cent of nitrobenzene in oil, (3) nitrobenzene in water, and (4) low-boiling fractions in charge stocks for the nitrobenzene plant.

Determination of 0 to 5 Per Cent of Nitrobenzene in Oil

Two materials in the plant contain nitrobenzene in concentrations of from 0 to 5 per cent: the extract and the raffinate. Two methods are presented for analyzing these materials. The first method involves the reduction of the nitrobenzene to aniline by titanous sulfate. It is accurate and reliable but requires 1 hour per determination and some

TABLE I. SUMMARY

Sample Taken	Where Taken (Figure 1)	Frequency of Sampling	Analysis Desired	Probable Concentration Range %	Analytical Method Used	Maximum Time for Analysis Min.
Raffinate	<i>A</i>	One sample per tank	Nitrobenzene	0 to 0.1	Titanous sulfate	60
	<i>B</i>	3 to 6 per day	Nitrobenzene	0 to 0.1	Pensky Martens flash	30
	<i>C</i>	For special purpose only	Nitrobenzene	0.1 to 1.0	Pensky Martens flash	30
	<i>D</i>	For special purpose only	Nitrobenzene	10 to 30	Specific gravity or distillation	60
	<i>E</i>	For special purpose only	Nitrobenzene	10 to 30	Specific gravity or distillation	60
Extract	<i>F</i>	For special purpose only	Nitrobenzene	50 to 90	Specific gravity or distillation	60
	<i>G</i>	For special purpose only	Nitrobenzene	50 to 90	Specific gravity or distillation	60
	<i>H</i>	For special purpose only	Nitrobenzene	0.1 to 1.0	Specific gravity or distillation	60
	<i>I</i>	One per day	Nitrobenzene	0 to 0.1	Pensky Martens flash	30
	<i>J</i>	One sample per tank	Nitrobenzene	0 to 0.1	Titanous sulfate	60
Recovered nitrobenzene	<i>K</i>	2 per month	Nitrobenzene	95 to 100	Distillation and freezing point	90
Water	<i>L</i>	3 to 6 per day	Nitrobenzene	0 to 0.2	Colorimetric	30
Charge stock	<i>M</i>	One sample per tank	Light oil	0 to 1.0	Flash difference or double distillation	90

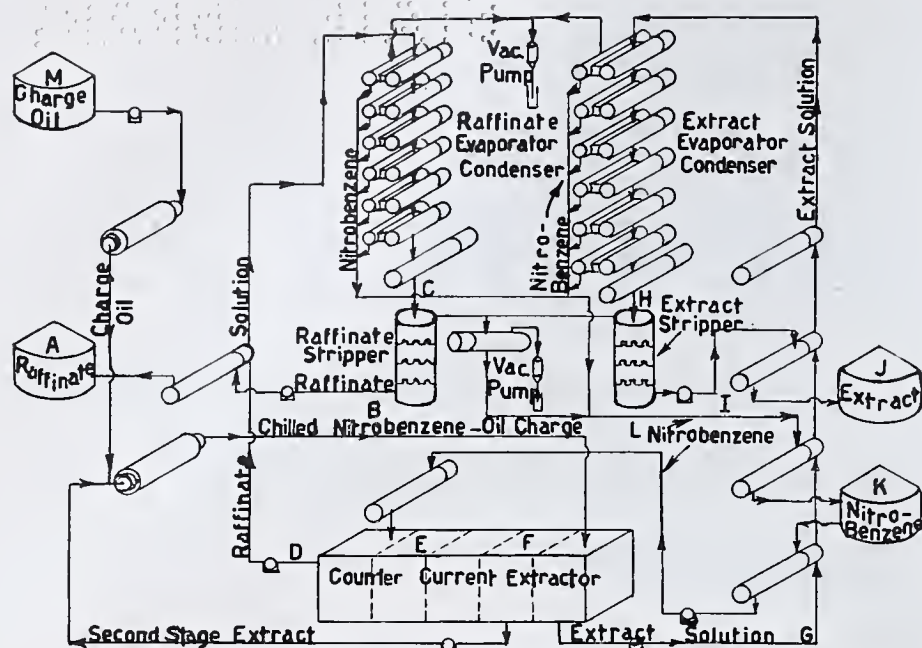


FIGURE 1

skill in manipulation; consequently it is used only to determine the nitrobenzene content of each tank of finished oil. The second method depends upon the fact that the presence of small amounts of nitrobenzene in a lubricating oil stock produces an appreciable lowering of the Pensky Martens closed-cup flash of the stock. This method is simple and rapid, and is used as a periodic check on plant operation.

TITANOUS SULFATE METHOD. In this method, described in a previous paper (1), a small sample of oil admixed with xylene, methyl alcohol, 40 per cent sulfuric acid, and standard titanous sulfate solution is boiled under an atmosphere of carbon dioxide. The nitrobenzene is reduced and the remaining titanous sulfate back-titrated with ferric alum, the titanous sulfate consumed in the reaction being the measure of the nitrobenzene present. Because titanous sulfate is oxidized in the presence of air it must be kept in an oxygen-free atmosphere at all times; hence the necessity for careful technic in this determination. When the proper technic is employed, the absolute error of the method varies from ± 0.01 per cent on samples containing up to 0.1 per cent of nitrobenzene to 0.2 per cent on samples containing 5 per cent of nitrobenzene. All results are calculated to a weight-per cent basis.

PENSKY MARTENS FLASH METHOD. With the aid of Figure 2 the Pensky Martens closed-cup flash point (A. S. T. M.

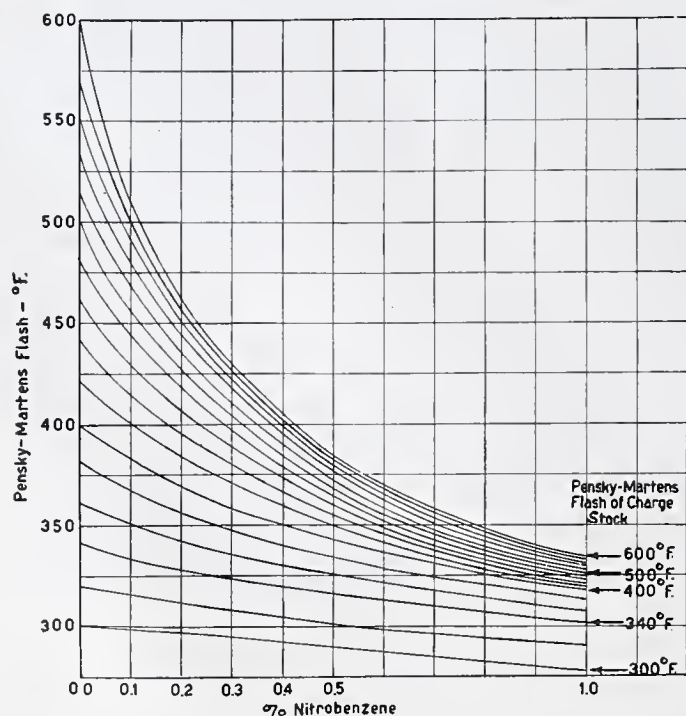


FIGURE 2

Designation D93-22) of an oil-nitrobenzene mixture may be compared with the flash point of the original stock and thereby used as a measure of the nitrobenzene content of the oil. Figure 2 is applicable for oils varying from 149 C. (300° F.) to 316° C. (600° F.) closed-cup flash, but is more accurate for oils having a flash point above 204° C. (400° F.). The series of curves shown were interpolated from many experimental data.

In using Figure 2, the curve corresponding to the flash point of the original stock, as indicated by the arrows, is selected. The point where this curve crosses the line representing the flash point of the mixture (read on the y axis) is read on the x axis as the weight-per cent of nitrobenzene in the mixture. The application of this method is limited to operation where the original charge oil has been properly stripped to eliminate light fractions, as evidenced by a small spread between the open- and closed-cup flashes, described in more detail below. If the closed-cup flash of the raffinate or extract differs from that of the charge, the closed-cup flash of the product in question should be used in evaluating its nitrobenzene content.

It will be observed from Figure 2 that this method will not indicate concentrations above 1.0 per cent. Its accuracy in the working range as based on test oil-nitrobenzene mixtures is given in Table II.

TABLE II. ACCURACY OF PENSKY MARTENS FLASH FOR DETERMINING NITROBENZENE

Nitrobenzene Present	Pensky Martens Flash of Original Stock	Pensky Martens Flash of Mixture	Nitrobenzene (Figure 2)	Deviation
%	° F.	° F.	%	%
0.01	495	485	0.02	+0.01
0.35	495	395	0.30	-0.05
0.05	440	430	0.03	-0.02
1.00	440	330	0.83	-0.19
0.05	400	390	0.05	0.00
0.50	400	350	0.40	-0.10
0.05	365	360	0.04	-0.01
1.00	365	310	1.00	0.00
0.01	305	305	0.00	-0.01
0.35	305	300	0.20	-0.15

Since this procedure is intended for rapid plant-control work, it has been found desirable to heat rapidly to about 149° C. (300° F.) in the case of high-flash oils and then adjust to the standard rate of heating prescribed in A. S. T. M. procedure D93-22.

Determination of 5 to 100 Per Cent of Nitrobenzene in Oil

While the methods given above are satisfactory for low concentrations of nitrobenzene in oil, their relative errors are high enough to preclude their use on samples coming from various points in the plant where the nitrobenzene content ranges from 5 to 100 per cent.

Two methods are presented for this concentration range. The first merely takes advantage of the wide difference between the specific gravity of oil and nitrobenzene. Because the specific gravity of the oil stock is usually known in plant operation, this method provides a simple and rapid control procedure. The second method may be used when the specific gravity of the oil is not known or when it is desired to isolate a sample of the oil from the nitrobenzene for physical property determinations. It consists of distilling the nitrobenzene from the oil under vacuum and measuring the weight of the residual oil. When a check on the oil boiling in the nitroben-

zene range is desired, this method may be supplemented by a freezing point determination on the nitrobenzene distillate.

SPECIFIC GRAVITY METHOD. The additivity of the specific gravities of nitrobenzene and oil on a volume basis was checked experimentally for a variety of light and heavy oils. This offered a simple means of estimating nitrobenzene concentration when the oil gravity was known. Accordingly, a series of charts was prepared relating the specific gravity of the nitrobenzene-oil mixture to the volume and weight-per cent of nitrobenzene. A range of from 0.8 to 1.02 in the specific gravity was covered and in order to insure the homogeneity of the mixtures all specific gravities are taken at 60° C. (140° F.) or 100° C. (212° F.) depending on the viscosity of the mixtures. The specific gravity of plant nitrobenzene was found to be 1.167 at 60° C. and 1.127 at 100° C. Both values are referred to water at 15.5° C. (60° F.).

VACUUM DISTILLATION AND FREEZING POINT. This method for determining the nitrobenzene content of an oil-nitrobenzene mixture consists of a vacuum distillation of a weighed charge of the mixture to a specified liquid temperature, after which the oil is stripped free of nitrobenzene with an inert gas, the residual oil weighed, and any oil distilling over with the nitrobenzene may be estimated from the freezing point of the distillate and added to the residual oil.

In most cases this procedure may also be used when it is desired to isolate a sample of the oil from the mixture for physical property measurements. Experimental work has shown that using a properly stripped light stock (400° F. flash point) a maximum of 0.6 per cent of oil based on the mixture distills with the nitrobenzene. When using stocks of 260° to 316° C. (500° to 600° F.) flash point 0.1 per cent or less distills. Physical properties on the residual oil may then be used for plant control except where a light stock is present in the mixture in low concentrations.

The apparatus is illustrated in Figure 3. *A* is a 2-liter balloon flask fitted with a Claisen head, *B*, *B* is electrically heated by wrapping with 550 cm. of No. 30 nichrome wire, insulated with asbestos and heated by 110-volt alternating current. *C* is a capillary tube for admitting carbon dioxide and preventing bumping. *D* is 0° to 300° C. thermometer, *E* a water-cooled condenser, *F* an adapter provided with vacuum and manometer outlets, and *G* a 1-liter balloon flask. This size of apparatus permits the distillation of 1-liter samples, which is desirable when physical properties are to be determined on the residual oil.

When only the nitrobenzene content of the mixture is desired, flask *H* (upper left insert, Figure 3) is preferred. This is a 250-cc. distillation flask with the side arm bent as shown in order to decrease entrainment and is equipped with an additional side neck fitted with a capillary tube for admitting carbon dioxide gas.

The freezing point apparatus (right insert, Figure 3) is made of two test tubes, one placed inside the other to form an air-jacketed freezing point tube. A convenient size for these tubes is 15 and 25 mm. in diameter, respectively. A thermometer calibrated in 0.1° C. over the range 0° to 6° C. is placed through cork in the inside tube and stirring is effected by a wire loop stirrer.

A charge of approximately 1000 grams is weighed to 0.1 gram into the weighed distilling flask, *A*. The flask is connected to the Claisen head and the system is evacuated to a pressure of 30 mm. A small stream of carbon dioxide bubbles is admitted to the flask to prevent bumping, and the oil is distilled at 30 mm. pressure until the liquid temperature reaches 220° C. (428° F.). At this point, the carbon dioxide rate is increased somewhat and heating is continued until a temperature of 250° C. (482° F.) is reached in order to strip the residual oil of nitrobenzene. The temperature is held at this point for 3 minutes, after which the oil should be free of nitrobenzene. The flask and contents are then cooled and again weighed. The residual oil in the flask represents the heavy oil in the sample. The same procedure is used in the distillation of 100-gram samples, using flask *H* instead of *A* and Claisen head *B*.

In order to determine the oil in the nitrobenzene overhead, a portion of this material is poured through the condenser and adapter in order to dissolve any oil remaining from the stripping procedure, the total distillate is mixed, and the air-jacketed test

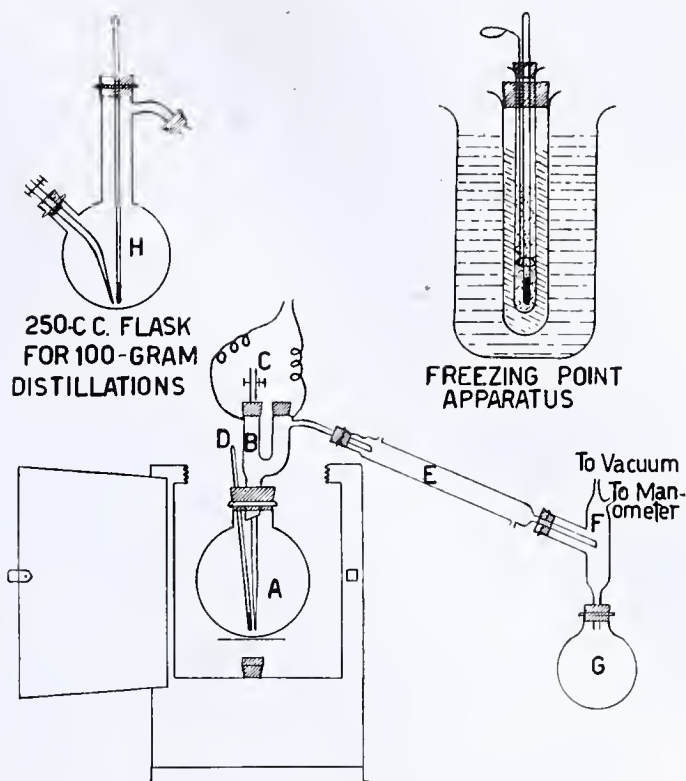


FIGURE 3

tube filled half full of this mixture. Two drops of water are then added to the test tube and the tube is fitted with the thermometer and stirrer. The liquid is stirred vigorously for a few moments in order to saturate the sample with water, then placed in an ice-and-water bath, and the freezing point determined.

The weight-per cent of light oil distilling with the nitrobenzene is approximated from the freezing point by the following formula:

$$\text{Weight-per cent of oil} = \frac{(5.13 - \text{freezing point } ^\circ \text{C.}) \times 165}{70} \times \text{weight-per cent of distillate.}$$

5.13° C. is taken as the freezing point of plant nitrobenzene, 165 is the experimentally determined molecular weight of oil distilling with nitrobenzene, and 70 is the freezing point constant (6) of nitrobenzene. The absolute error of the method is about ± 0.5 per cent.

Determination of Nitrobenzene in Water

While the condensed steam from the vacuum pumps and the strippers of the nitrobenzene plant will retain less than 0.2 per cent of nitrobenzene, even this small amount can be economically recovered. This is accomplished by vaporizing about 10 per cent of the water, which on condensation throws out nitrobenzene while the water condensate saturated with nitrobenzene is reprocessed. Practically all the nitrobenzene will appear in this distillate and the remaining 90 per cent of the water can be discarded.

The nitrobenzene content of the stripped water bottoms is determined by a colorimetric method, based on the reduction of nitrobenzene to aniline which forms a colored product on reaction with sodium hypochlorite. The color intensity is a measure of the nitrobenzene content of the water examined. This method is a modification of Evolve's test for aniline (2).

REAGENTS AND APPARATUS: 1 to 1 hydrochloric acid; 32 per cent hydrochloric acid; 15 per cent potassium hydroxide; 15 per cent solution of cobaltous chloride crystals ($\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$) containing 25 cc. of 32 per cent hydrochloric acid per liter; 7.5 per cent solution of ferric chloride crystals ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) containing 25 cc. of 32 per cent hydrochloric acid per liter; sodium hypochlorite solution containing 0.11 per cent of available chlorine; powdered zinc; solutions of nitrobenzene in water, 0.01, 0.03, 0.04, and 0.05 per cent by weight; one daylight lamp assembly; a test-tube condenser made of a test tube that will fit the neck of a 250-cc. Erlenmeyer flask and provided with a cork carrying water inlet and outlet tubes.

PERMANENT COLOR STANDARDS. The permanent color standards are prepared by taking the quantities of 7.5 per cent ferric chloride solution and 15 per cent cobaltous chloride solution indicated in Table III, and making up to 100 cc. in a Nessler tube with water containing 25 cc. of 32 per cent hydrochloric acid per liter.

TABLE III. PREPARATION OF COLOR STANDARDS

Standard No.	7.5 Per Cent FeCl ₃ Solution	15 Per Cent CoCl ₂ Solution
	Cc.	Cc.
1	10.0	0.7
2	7.5	1.1
3	7.0	1.9
4	11.0	4.0
5	12.0	5.5
6	33.0	6.0

The Nessler tubes containing these solutions should be corked whenever not in use. They should be checked monthly against standard nitrobenzene solutions. The color standards are considered satisfactory if they match the colors produced by samples of known nitrobenzene content according to Table IV.

TABLE IV. CHECKING OF COLOR STANDARDS

Size of Sample	Nitrobenzene in Sample	Standard Which Should Check Color Produced
Cc.	%	
10	0.01	1
20	0.01	2
10	0.03	3
10	0.04	4
10	0.05	5
20	0.03	6

PROCEDURE. If the sample contains sediment or oil, it should be filtered. The amount of sample taken will depend upon the concentration expected (Table V). The required amount is diluted to 25 cc. with distilled water in a 250-cc. Erlenmeyer flask which is provided with the test-tube water-cooled condenser extending into the flask about 11 cm., and 15 cc. of 1 to 1 hydrochloric acid are added. The solution is brought to a boil, approximately 0.3 gram of zinc dust added, and the condenser replaced as quickly as possible. The solution is allowed to stand for exactly 2 minutes and is then filtered, cooled in ice water, and 5 cc. of sodium hypochlorite (0.11 per cent of available chlorine) are added, followed by 50 cc. of 15 per cent potassium hydroxide solution. The solution is again cooled in ice water, filtered, and made up to 100 cc. in a Nessler tube which is placed in the tube rack. The color of this solution is compared, at the end of 30 minutes from the time when the sodium hypochlorite was added, with the permanent color standards by looking down through the full length of the tubes, a porcelain plate at the bottom of the rack being illuminated by a daylight lamp. Check determinations should be run.

Table V gives the weight-per cent of nitrobenzene for specified sizes of samples when the color developed corresponds to one of the color standards.

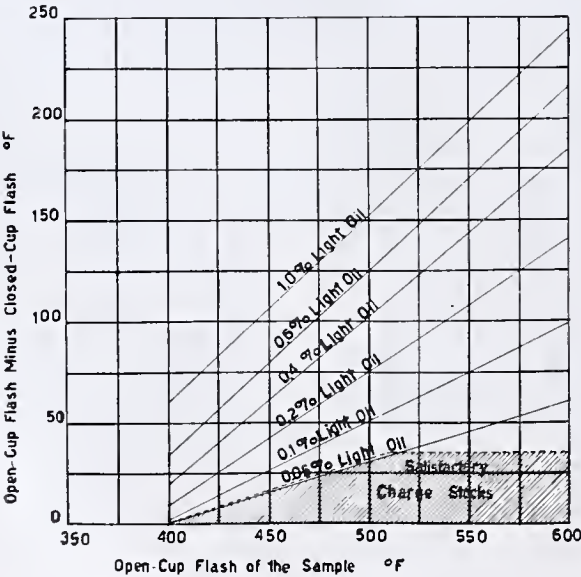


FIGURE 4

TABLE V. WEIGHT-PER CENT OF NITROBENZENE IN WATER

Volume of Sample Taken	Standard No.					
	1	2	3	4	5	6
Cc.	%	%	%	%	%	%
20	0.005	0.01	0.015	0.02	0.025	0.03
10	0.01	0.02	0.03	0.04	0.05	0.06
5	0.02	0.04	0.06	0.08	0.10	0.12
2.5	0.04	0.08	0.12	0.16	0.20	0.24

The accuracy of the method is indicated by the experimental data in Table VI.

TABLE VI. ACCURACY OF COLORIMETRIC METHOD FOR ESTIMATING NITROBENZENE IN WATER

Sample	Nitrobenzene Added	Nitrobenzene Estimated
	%	%
1	0.005	0.005
2	0.02	0.017
2	0.02	0.018
2	0.02	0.020
3	0.06	0.058
3	0.06	0.054
3	0.06	0.056
4	0.10	0.10
4	0.10	0.09

Charge Stock Analysis

In all solvent-refining processes it is necessary either to avoid contamination of the solvent with lighter fractions which may be brought into the system by the oil charge or else to resort to special methods of separating the oil and solvent.

If the oil charged to the plant contains fractions of the same volatility as nitrobenzene, in stripping solvent from oil some of the oil will be taken off with the solvent and so contaminate the latter with a nonselective diluent.

In the nitrobenzene process the introduction of contaminating oil fractions into the system is preferably and simply avoided by proper steam-stripping of the oil charge in the initial distillation of the crude. Experience has shown that less than 0.05 weight-per cent of light fractions in the oil charge gives negligible contamination of the solvent nitrobenzene. Consequently, oil charge stocks are examined for light oil content for which two test methods are available. The first method, for use on stocks having an open-cup flash point (A. S. T. M. Designation D92-33) above 232° C. (450° F.) depends upon the difference between the open- and closed-cup flash points of the sample, while the second method, for use on stocks having an open-cup flash of less than 232° C. (450° F.) consists of a double vacuum distillation and a direct measurement of the light oil present.

FLASH DIFFERENCE METHOD. Owing to the presence of air currents which carry away small amounts of vaporized oil, the open-cup flash point of a high-flash oil is only very slightly affected by the presence of oil boiling in the nitrobenzene range in concentrations up to 1.0 per cent. On the other hand, the Pensky Martens closed-cup flash point is very sensitive to small amounts of light oil. If no light oil is present the two flashes will be identical within the limits of experimental error (±5° F. for each flash).

This phenomenon has been utilized in the determination of low boiling oil in charge stocks to the nitrobenzene plant. It is very well suited for this purpose, because both the amount of oil that will distill with the nitrobenzene and the effect that it will have on the closed-cup flash point of the stock are roughly proportional to the volatility of the oil. Thus the only assumption necessary regarding the characteristics of the light oil is that its initial boiling point is not far below that of nitrobenzene, which has been the case in a variety of actual stocks examined. This assumption is necessary only because the lower boiling oil will tend to vaporize from the nitrobenzene in plant operation and be ejected from the system

through the vacuum pumps, thus preventing its accumulation. Figure 4 correlates the per cent of low-boiling oil with the difference between the open- and closed-cup flashes for mixtures of varying open-cup flashes. Lines were drawn representing various percentages of light material. For a given concentration of light oil the difference between the open- and closed-cup flashes is much greater in the case of high open-cup flashes than for low ones, and for this reason the method is not satisfactory when the open-cup flash is below 232° C. (450° F.). Charge stocks which do not fall in the shaded area on Figure 4 are not acceptable for the nitrobenzene plant.

Because of the $\pm 5^{\circ}$ F. errors that cannot be avoided in the flash determinations, check values should be determined in order to obtain the best accuracy. Table VII is typical of the accuracy that can be obtained. The light oil used for the data in this table had a 50 per cent boiling point of 229° C. and an average molecular weight of 196.

TABLE VII. ACCURACY OF FLASH DIFFERENCE METHOD

Weight- Per Cent of Light Oil Added	Open-Cup Flash ° F.	Closed-Cup Flash ° F.	Open-Cup Minus Closed-Cup Flash	Weight- Per Cent of Light Oil Found	Deviation
0.005	555	555	0	0	-0.005
0.02	560	535	25	0.02	0.00
0.045	550	510	40	0.04	-0.005
0.045	560	500	60	0.07	+0.025
0.10	550	485	65	0.08	-0.02
0.20	550	435	115	0.25	+0.05
0.23	545	440	105	0.20	-0.03
0.25	560	440	120	0.24	-0.01
0.50	540	390	150	0.50	0.00
0.90	555	370	185	0.80	-0.10

DOUBLE DISTILLATION. For stocks having an open-cup flash of 232° C. (450° F.) or lower, the preferred procedure is the double-vacuum distillation which gives a direct measure of the light oil present. This method is more accurate but more time-consuming than the flash difference method.

The apparatus used for this method is very similar to that illustrated in Figure 3 for determining nitrobenzene in oil. The first distillation is carried out in the large-scale apparatus differing from Figure 3 only in that a 3-liter flask is used instead of a 2-liter flask, and the distillate is collected in a 100-cc. graduate instead of the 1-liter flask shown. The second distillation is carried out in a small apparatus using a 100-cc. Claisen flask, a small water-cooled condenser about 20 cm. long and inclined at an angle of 45°, and a small adapter similar to that shown in

Figure 3, and the distillate is collected in a 10-cc. graduate calibrated in 0.1-cc. intervals. 0° to 300° C. thermometers are used in both distillations.

When the apparatus has been assembled, a charge of about 1300 grams of the stock to be examined is placed in the balloon flask, connections and stoppers are painted with collodion or celluloid solution, and the system is evacuated to 10 mm. or less. Carbon dioxide gas is admitted through the capillary tube at such a rate that if the source of vacuum is shut off the pressure in the system will fall at the rate of about 60 mm. per minute. This corresponds to a free gas rate of about 150 cc. per minute.

Under these conditions 50 cc. of the oil are distilled into the graduate, keeping the condenser temperature near that of the room. The liquid temperature in the still should never be allowed to rise above 300° C. (572° F.) in order to prevent cracking of the oil, and it is advisable to keep the temperature as far below this point as is practical by reducing the pressure below 10 mm. The distillation is continued until 50 cc. have been taken overhead, but in no case is a temperature of 300° C. exceeded. The distillate is then redistilled in the small set-up.

In the second distillation the pressure is maintained at 10 mm. and the material distilled slowly until the vapor temperature reaches 152° C. (305° F.). The condenser is allowed to drain for 5 minutes and the volume of distillate read in the graduate to the nearest 0.1 cc. This volume represents the quantity of low-boiling oil in the weighed charge and may be converted directly to a weight percentage basis by assuming a specific gravity of 0.8 for the distillate. If the weight-per cent of low-boiling oil is more than 0.05 per cent, the stock is not acceptable for nitrobenzene extraction.

The absolute error of this method is ± 0.02 per cent.

Acknowledgment

The authors wish to express their appreciation to J. H. Boyd, Jr., and W. A. Myers for their helpful suggestions in the preparation of this paper, to their laboratory associates for assistance in the experimental work, and to The Atlantic Refining Company for permission to publish these results.

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RECEIVED October 10, 1935.

Determination of Radium in Carnotite and Pitchblende

L. D. ROBERTS, University of Southern California, Los Angeles, Calif.

RADIUM is determined electroscopically by means of radon which is introduced into an electroscope chamber. Using a Lind electroscope the radium content of carnotite or pitchblende can be estimated accurately.

In the first method proposed the ore is fused with a mixture of sodium and potassium carbonates in a platinum boat (3), the fusion dissolved in nitric acid, and the radon collected in an electroscope chamber. The objection that the fusion sometimes does not dissolve, but remains hard and glassy in the boat, is met by chilling the fusion suddenly by partly submerging the boat immediately in cold water on removal from the flame or furnace. The fusion draws away from the boat and leaves the boat while in the boiling nitric acid. In every case all the radon is removed, and the results are not low. This method gives excellent results.

Barker proposed the bisulfate fusion method (1). Later

he suggested the phosphoric acid method (2), stating that in the bisulfate method heating the fusion to drive out the radon breaks the test tubes by expanding the fusion. When the fusion is rolled on the side of the tube as the fusion cools, the Pyrex tubes are never broken.

All these methods give good results, and may be applied to any product from carnotite or pitchblende containing radium. Scott (4) gives methods for the analysis of radioactive solutions.

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RECEIVED November 19, 1935.

A Method of Analysis for Fluoride

Application to Determination of Spray Residue on Food Products

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THE widespread use of fluorine compounds as insecticides and the establishment by the Federal Government of a tolerance, or upper limit to the amount of added fluorine which may be present on or in foodstuffs, have combined to stimulate interest in the quantitative determination of minute amounts of this element. Consequently, several dozen publications on various methods of analysis have recently appeared. Work on the subject was undertaken in this laboratory in connection with a study of the amounts of arsenic, lead, and fluorine which occur on fruit sprayed in various ways for the control of the codling moth in California.

Preliminary experiments with several suggested methods indicated the superiority of the reaction between fluoride and thorium ions in the presence of an indicator sensitive to excess thorium. Accordingly, an intensive investigation has been made of Armstrong's (1) modification of the Willard and Winter (14) method which involves the titration in 50 per cent alcohol of fluoride ion with standard thorium solution in the presence of sodium alizarin sulfonate. For comparison, the Sanchis (9) method adapted from that of Thompson and Taylor (12), which depends upon the bleaching effect of fluoride ion upon a zirconium-alizarin complex, has been used in certain cases.

Titration with Standard Thorium Solutions

Standard fluoride solutions were prepared from recrystallized c. p. sodium fluoride. Their accuracy was checked by the standard method of precipitation as CaF_2 (10). Stock solutions were made 0.05 *M* and dilutions to lower concentrations as needed. Very dilute solutions of sodium fluoride, such as 0.001 *M*, decrease in strength if kept in glass vessels, but if the containers are lined with paraffin the concentration remains constant for long periods. Thorium solutions, approximately 0.05 *M*, were made from c. p. thorium nitrate and were standardized by precipitating as thorium oxalate, heating, and weighing as the dioxide. The solutions were then diluted to 0.01 *M* or 0.001 *M* for use. These dilute solutions were made at intervals of 2 to 3 weeks, though they appear to be stable for longer periods. Comparison of the dilute standard solutions of fluoride and thorium by the method to be described gave excellent agreement.

The first experiments followed the procedure of Armstrong. It was soon found that three factors must be carefully controlled in order to obtain duplicable results: the volume of indicator added, the intensity of color in the blank and unknown, and the acidity. The first two are inseparably connected, for the more indicator used the smaller is the volume of thorium solution required to produce a given intensity of color in the blank. As judged by the eye, the pink color is most sensitive to changes in the amount of thorium added when its intensity is very low. It is not advisable to use large amounts of indicator in order to reduce the thorium needed in the blank, because the pink tint is masked by the yellow color of the indicator where much is used in acid solution. Summarizing a large number of experiments, it may be said that when a volume of 50 cc. is used for the blank, 0.040 cc. of a 0.05 per cent aqueous solution of sodium alizarin sulfonate—i. e., the concentration of the indicator in the solution is 4×10^{-5} per cent—plus 0.040 to 0.070 cc. of 0.001 *M* thorium solution gives a faint pink color which is very suitable for matching and is very sensitive to thorium ion. For other volumes in the blank, proportional amounts of the reagents should be used. It is advisable to run a fresh blank with each unknown, for the color slowly becomes more intense as the

solutions are allowed to stand. This is undoubtedly due to slowness of one or more of the reactions which are involved in the equilibrium between Th^{++++} , F^- , and sodium alizarin sulfonate. In the somewhat analogous method used by Thompson and Taylor (12) and by Sanchis (9)—i. e., the bleaching of red zirconium alizarin sulfonate by fluoride—the solutions are brought to boiling to hasten the establishment of equilibrium, which is said to require 48 hours in the cold.

Effect of Acidity and Use of Buffer

Previous workers have paid scant attention to the acidity of the solution during titration. The usual directions have been to destroy the pink color with 1 to 50 hydrochloric acid solution (0.24 *N*) before adding the thorium solution. For precise work, however, the acidity is important. If the solution is decolorized, but no excess acid is added, extremely low values are obtained. The addition of one drop of acid in excess usually is satisfactory, but larger amounts of acid lead to the use of too much thorium solution (Table I). Vanselow (13) of the Citrus Experiment Station has found the same effect for excess acid. While it is possible to control the acidity by careful use of dilute hydrochloric acid, the use of a buffer offers advantages. Preliminary experiments, using the indicator bromophenol blue, indicated that the most desirable pH was approximately 3.5. In order to give this pH at half neutralization—i. e., at maximum buffering power—a buffer acid must have a *paK* of the same magnitude. The data of Jukes and Schmidt (5) show that *paK* for acetic acid is increased by about 0.7 in passing from water to 50 per cent alcohol. Hence, it seemed probable that the *paK* of the related acid, monochloroacetic, which is 2.8 in water, would be approximately 3.5 in a mixture containing equal parts of commercial 95 per cent alcohol and water—i. e., about 48 per cent alcohol.

The behavior of chloroacetic acid in 48 per cent alcohol was investigated by determining the pH of solutions containing 2.00 cc. of 1 *M* monochloroacetic acid solution and varying volumes of 1 *M* sodium hydroxide solution in a total volume of 100 cc. A hydrogen electrode was used and a glass electrode was standardized in the same solutions. The results are given in columns 1 and 2 of Table I.

TABLE I. pH OF CHLOROACETIC ACID-SODIUM HYDROXIDE BUFFERS (0.02 *M*) IN 48 PER CENT ALCOHOL

Molecular Ratio Acid:Base	pH	Relative Volumes of Th^{++++} Solution	
		Blank at constant buffer ratio 0.5	Blank and test solu- tion at same buffer ratio, volume at 0.5 taken as unity
1:0.2	2.95	1.411	1.050
1:0.3		1.292	1.000
1:0.4	3.39	1.171	1.000
1:0.5		1.000	1.000
1:0.6	3.73	0.975	1.000
1:0.7		0.903	0.957
1:0.8	4.17	0.768	0.811

A plot of these results shows that at half neutralization the pH is 3.55, which is accordingly the *paK* value of chloroacetic acid in equal parts by volume of water and commercial ethyl alcohol. The corresponding dissociation constant, *K_a*, is 2.8×10^{-4} . It was necessary to prove that this buffer is able to maintain a constant pH during the titration with tho-

rium solution. Typical titrations were made with varying amounts of fluoride ion present and the various buffer mixtures present at 0.02 *M* concentration. The hydrogen electrode did not function in the presence of the indicator, but the glass electrode gave very steady potentials exactly equal in all cases to those previously obtained in the buffer solutions alone. Since it may be necessary to analyze samples containing considerable acid or base, the most desirable procedure is to bring the solution to the approximate transition point of the indicator with dilute acid or base—e. g., 0.05 *N* hydrochloric acid or sodium hydroxide—before adding the buffer solutions.

The third column of Table I shows how greatly the volume of thorium solution required to obtain an end point is altered at various pH values of the test solution when the blank is held at a constant buffer ratio of 0.5. It is obviously not possible to obtain accurate results except over a very narrow pH range. In the last column it is shown that when the blank and test solutions have the same pH a much wider range is allowable. The buffer ratio 0.5, at which the pH is 3.55, is seen to be in the middle of the favorable range. The above results at once raise the question of how greatly the pH of a 48 per cent alcohol solution varies when treated with a dilute solution of hydrochloric acid as in the ordinary adjustment of acidity according to the directions of Willard and Winter (14) and of Armstrong (1). For the sake of greater delicacy, tests were made in which 0.05 *N* hydrochloric acid was used instead of the 0.24 *N* (1 to 50) recommended by the above workers, so that the changes in pH were smaller than with corresponding volumes of stronger acid solution. The results are given in Table II. A comparison of Tables I and II will show what very serious errors result from the inevitable inaccuracy involved in trying to add one drop of 0.24 *N* acid in excess to an unbuffered solution.

TABLE II. EFFECT OF pH UPON COLOR OF SODIUM ALIZARIN SULFONATE IN 50 PER CENT COMMERCIAL ALCOHOL

Volume of Acid	0.000	0.030	0.045	0.075	0.085	0.145
pH	8.8	7.2	6.3	5.2	4.8	4.1
Color	Pink	Pale pink	Very pale pink	Very pale yellow	Pale yellow	Yellow

In Table II is shown also the effect of pH upon the color of sodium alizarin sulfonate in 50 per cent commercial alcohol as determined by adding 0.05 *N* hydrochloric acid in small increments to 50 cc. of solution containing 0.04 cc. of 0.05 per cent solution of the indicator and made slightly basic at the start. The pH was determined with the glass electrode. Kolthoff and Furman (6) state that the color changes occur in water in the pH range 3.7 to 5.2.

It is obvious that the equilibrium between the acidic and salt forms of the indicator occurs in the alcoholic solution in a more alkaline range than in water, which is in agreement with the behavior of most weak acids.

Accuracy and Delicacy of the Titration

The procedure described above has been used many times in titrations of standard solutions of sodium fluoride. The range of concentration before addition of alcohol was from 0.00012 *M* to 0.0016 *M*—i. e., 2.3 to 30.4 p. p. m. as fluorine. The total fluoride in 25 cc. therefore varied from 57 to 760 γ . The maximum errors were +3.7 and -2.7 per cent, with an average error of -1.0 per cent. No distinct variation in percentage error occurred as the concentration of fluoride was varied over this range. This is a somewhat smaller average error than that of -1.7 per cent which may be calculated from the data of Willard and Winter (14) for the titration according

to their procedure of standard fluoride solutions ranging in concentration from 0.0004 *M* to 0.004 *M*.

The limiting factor seems to be the slowness with which equilibrium is reached near the end point. As mentioned before, the color of the blank slowly becomes more intense. For larger amounts of fluorine the uncertainty thus introduced is negligible, but with small amounts the unavoidable difference in age of the blank and test solutions may cause an appreciable error. This may be eliminated to some extent by using a second blank which is matched against the sample. The average of the volumes of thorium solution used in the two blanks is used. Attempts to speed up the attainment of equilibrium by running the titrations at 60° C. were not successful, for the red thorium alizarin sulfonate was rapidly coagulated.

There is no *a priori* reason for using a volume as large as 50 cc. for titration, so a series of experiments was made in which the volume was made up to 5 cc. Small matched test tubes were used and it was found easy to obtain the same accuracy with 6 to 90 γ of fluoride as with the larger amounts in 50 cc.

For purposes of comparison with an entirely different method of analysis two series of solutions from fruits and vegetables treated with fluoride sprays were tested by the present method and by that of Sanchis (9). Over the range from 4 to 400 γ of fluorine in 25 cc. the latter method gave results which average 3.6 per cent higher than those obtained by titration. In many cases agreement was very close, but occasionally samples run by the Sanchis method were quite different in color from the standards.

Interfering Substances

When fluoride is present in solutions containing possible interfering ions or compounds, the recommendation is usually made that it be isolated by distillation from perchloric or sulfuric acid solution. Under such conditions, however, the halides, nitrate, sulfite, and other rarer contaminants are also distilled and the possibility always exists that nonvolatile substances will be carried into the distillate as spray. For these reasons a study has been made of the effects of a number of ions at various concentrations in order to determine, at least approximately, the maximum amounts which may be tolerated in the fluoride solution. This depends, of course, upon the amount of fluoride used and upon the accuracy desired. The tests were made with 1.00 cc. of 0.003 *M* sodium fluoride solution in a total volume of 50 cc. Varying amounts of the sodium salts of each ion were added and the pH was adjusted as described above. In Table III the concentrations are stated at which an appreciable increase in volume of thorium solution was required. The precise concentrations at which interference first develops is accordingly a little lower than the figures given. If a stronger pink color is taken as the end point of the titration, interference occurs at lower concentrations.

TABLE III. EFFECT OF VARIOUS IONS UPON TITRATION OF FLUORIDE WITH THORIUM

Ion	Concn. for Appreciable Effect	Ion	Concn. for Appreciable Effect
Halogens	0.1 <i>M</i>	AsO ₃ ---	1×10^{-4} <i>M</i>
NO ₃ ---	0.1 <i>M</i>	SO ₄ ---	1×10^{-6} <i>M</i>
ClO ₄ ---	0.1 <i>M</i>	AsO ₄ ---	1×10^{-6} <i>M</i>
SO ₃ ---	0.002 <i>M</i>	PO ₄ ---	$<1 \times 10^{-6}$ <i>M</i>

The only halogen ion which is likely to be encountered at concentrations high enough to interfere is chloride. It was found, however, that by adding an equal amount of it to the blank the effect is made equal in sample and blank and hence no error results. Similar observations concerning the effects

of chloride and sulfate have been made by Sanchis (9) and of chloride and nitrate by Bowes (3). The tests with sulfite were complicated by the fact that all available so-called c. p. samples were contaminated with sulfate. When this was removed by adding excess barium, an error was introduced on account of the formation in the alcoholic solution of insoluble or slightly ionized barium fluoride. It is probable that this compound will yield its fluoride to thorium ion, but the equilibrium is established too slowly for practical purposes. But by precipitation of the sulfate with the minimum amount of barium a solution of pure sulfite was obtained and its effect determined.

Interference by sulfate at such low concentration is surprising, since thorium sulfate is soluble in water to the extent of approximately 1 per cent. However, the conductivity measurements of Barre (2) show that a 0.001 *M* solution in water is by no means completely dissociated, and it is to be expected that weakness of the salt will be greatly increased in the presence of alcohol. Phosphate appears to react quantitatively with thorium. Interference from this ion was noted previously by Reynolds (7).

It is possible to prepare a solution of fluoride free from the most harmful ions by distillation as hydrofluosilicic acid according to the procedure of Willard and Winter (14). Either perchloric or sulfuric acid may be used, but the serious effects produced by the slightest trace of sulfate carried over as spray, or volatilized if the temperature gets too high, provide an argument in favor of perchloric acid. Certain differences in the behavior of the two acids have been noted by Shuey (11) when organic matter is present. Some lots of c. p. sulfuric acid contain a volatile impurity which greatly increases the volume of thorium solution required to produce a light pink color with the indicator. Its nature has not been determined, but it can be removed completely by boiling the concentrated sulfuric acid vigorously for a few minutes. Only a small part of this effect is due to fluoride in the sulfuric acid. Data on this are given below.

Preparation of Samples for Analysis

This paper is not primarily concerned with the practical analysis of various materials which contain fluorine, since that phase of the investigation is to be reported elsewhere. However, certain data and observations are appropriate here. In agreement with other workers it has been found that organic matter is destroyed most satisfactorily by heating in a muffle furnace. Vegetable or fruit material should be divided very finely and mixed intimately with a known weight of high-grade calcium hydroxide powder in a porcelain dish. Sufficient reagent must be used to maintain a basic condition throughout the rest of the process. Two grams are sufficient for 50 to 100 grams of the numerous kinds of fruits and vegetables so far investigated.

After thorough drying, first on a water bath and then on a low-temperature sand bath until slight charring is noticeable, the sample is placed in a muffle furnace and ashed. The results of a study of the effects of different furnace temperatures will be discussed below. Forty cubic centimeters of a 50 per cent solution of the previously boiled and cooled sulfuric acid and 0.5 gram of fine silica are added to a 250-cc. distilling flask equipped with trap and condenser and the ash is quantitatively introduced. The porcelain dish sometimes retains a portion of the ash. To insure the removal of all fluorine the dish is treated for several minutes with a few cubic centimeters of sulfuric acid which is then added to the distilling flask. A few cubic centimeters of distilled water are placed in the receiving flask in order to cover the outlet of the condenser. The distilling flask is heated with a Bunsen burner and an auxiliary flask filled with distilled water is heated simultaneously and steam is passed from the latter vessel into the distilling flask. By regulation of the two burners it is easily possible to hold the temperature of distillation at any desired point.

The results of distillations at various temperatures may be summarized as follows: Below 110° C. very little fluoride is volatilized; from 110° to 130° volatilization is increasingly efficient but is not complete enough with reasonable volumes of distillate; above 130° up to the temperature at which phosphates and sulfates may be distilled, the hydrofluosilicic acid is rapidly volatilized; 140° C. was chosen as the most satisfactory temperature. When the above method of distillation was applied to a large number of ash samples from fruits and vegetables an average of 96.7 per cent of the total fluorine which could be volatilized was recovered from the first 150 cc. For practical purposes distillation of 200 cc. was found to reduce the loss to a negligible point. Similar results have been obtained by Vanselow (13) who has used an analogous method of distillation. Winter and Butler (15) found that only 50 to 75 cc. need be distilled from perchloric acid solution. The observation of Reynolds (7) that the siliceous coating which forms on the inside of the distilling flask holds back fluoride from solutions rich in that element and liberates it later to samples deficient in fluorine, was also noted in the present work; so the removal of such films with alkali at frequent intervals was adopted as a standard procedure.

A series of runs in which a known amount of sodium fluoride was added to 50-gram lots of crushed ripe apples was made in order to test the accuracy of the whole method and in particular the effect of burning at different temperatures. A solution of sodium fluoride containing 1785 γ of fluorine was added to each sample and the burning, distillation, and titration were carried out as described before. The results for four different temperatures of the muffle furnace and lengths of time in it are given in Table IV. All temperatures were determined with a calibrated chromel-alumel thermocouple and millivoltmeter.

TABLE IV. EFFECT OF TEMPERATURE AND TIME IN MUFFLE FURNACE

Temperature of Furnace ° C.	Time Min.	Appearance of Ash	Recovery of Fluorine %
520	120	Dark	86.1
620	60	Light	93.7
720	20	Dark	97.3
820	10	Dark	75.2

These recoveries of added fluorine agree closely with the results of similar experiments by Reynolds et al. (8) and Winter and Butler (15). The serious loss in only 10 minutes' heating at 820° C. is particularly striking. Since the lime used to "fix" the fluoride during drying and ashing of the sample contained some fluoride as an impurity, a series of runs was made with different amounts of calcium hydroxide carried through the entire process. From the consistent results obtained allowance could be made for the fluoride in any amount of lime plus the standard amount of sulfuric acid and silica. Various lots of supposedly c. p. calcium hydroxide were found to differ in fluoride content from approximately 30 parts per million to nearly 100. For most purposes it does not seem necessary to prepare fluorine-free lime as recommended by Dahle (4). Various lots of c. p. sulfuric acid differ considerably in fluoride content, four bottles varying from a minimum of 0.3 to a maximum of 19 parts per million. Previous workers have attributed the failure to secure complete recovery of fluoride added to organic matter to either loss during ashing or incomplete volatilization. The present work indicates that loss during ashing is much more likely to explain the discrepancy. However, it is possible that the reactions which form complex fluorides that are stable in hot acid solution occur only when ashing is done at a high temperature. For this reason and in the hope of overcoming all difficulties connected with the use of a muffle furnace, a method of ashing based upon combustion in oxygen is now being studied.

Summary

The estimation of fluoride by titration with standard thorium solution in the presence of sodium alizarin sulfonate as indicator has been studied. The most favorable procedure includes the use of the indicator at a concentration of 4×10^{-5} per cent, in a total volume of 50 cc., titration to match a blank in which the end point is taken at a very light pink shade, and careful regulation of the pH in both blank and sample, the most favorable pH being 3.5. This latter condition is readily met by the use of the buffer system of sodium hydroxide and chloroacetic acid at a ratio of 0.5 and total concentration of 0.02 M. The dissociation constant of chloroacetic acid in 50 per cent commercial alcohol has been found to be 2.8×10^{-4} . Sodium alizarin sulfonate in this alcoholic solution acts as an indicator for hydrogen ion over the pH range 4.8 to 7.2 instead of 3.7 to 5.2 as in water. In a volume of 50 cc. an average accuracy of 99 per cent has been secured with known amounts of fluoride ranging from 57 to 760 γ of fluorine. With 5-cc. volumes approximately the same accuracy is possible with 6 to 90 γ of fluorine.

Data are given regarding the concentrations at which several interfering ions have an effect. The most serious of these are sulfate, arsenate, and phosphate, which fortunately are left behind when the fluoride is distilled as hydrofluosilicic acid. Sulfuric acid is entirely suitable for the distillation and a volume of 200 cc. distilled at 140° C. accounts for all but a trace of the fluoride. In the ashing of fruit samples containing fluoride for distillation it is very important not to allow the temperature to reach above 800° C., for loss is then excessive. Allowance must be made for the fluoride contained in the lime which is added to the sample before ashing. Re-

covery of fluoride added to apple pulp was 97.3 per cent under the most favorable conditions.

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Iodometric Determination of Copper

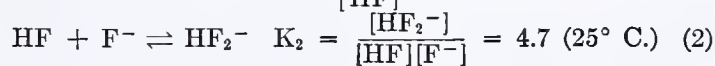
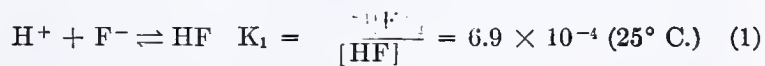
Adjustment of Hydrogen-Ion Concentration

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PARK (3) has recently described a method of determining copper in the presence of ferric iron and arsenic acid. By his method an iodometric titration is carried out in a solution containing ammonium bifluoride and potassium biphthalate. He states that the purpose of the bifluoride is to suppress the action of the ferric iron on potassium iodide, and that the biphthalate forms a buffer solution in which the pH is about 4.0, a value sufficiently high to cause no appreciable oxidation of iodide by the arsenic acid.

The problem of pH adjustment can be best understood if we consider the technic involved in the process. After decomposition of the ore with mineral acid, sufficient ammonium hydroxide is added to neutralize the excess mineral acid, arsenic acid, etc., precipitate the iron, convert the copper to the cupric ammonia complex, and produce a slight odor of ammonia. The bifluoride and biphthalate are then added. It is assumed that if the proper amount of biphthalate is added, the concentrations of phthalate and of biphthalate will be such as to produce an effective buffer solution at the pH desired. It is evident that an effective buffer action is necessary to allow for a reasonable variation in the amounts of excess ammonium hydroxide and of the other substances which react with the weak acid. In this process the possibility of the bifluoride's acting as a buffer evidently has been overlooked. Hudleston and his co-workers (1) have shown

that hydrogen fluoride in its aqueous solutions undergoes the following equilibria:



The ionization constant of biphthalate at 25° C. is 3.1×10^{-6} . To obtain a pH of 4.0, the ratio of concentrations of biphthalate to phthalate should be about 32 to 1, while the ratio of concentrations of hydrofluoric acid to fluoride should be about 1 to 7. At this pH the hydrofluoric acid should be a much more effective buffer than the biphthalate, and the pH at which it has maximum buffer efficiency is about 3.2. It seems reasonable to suppose, therefore, that it should be practicable to add such an amount of bifluoride that the concentrations of fluoride and of hydrofluoric acid formed would be sufficient not only to produce the ferric complex but also to yield simultaneously a buffer solution at a pH between 3 and 4.

It is the purpose of the present paper to show that under the conditions described by Park the pH at the end point is nearer 3.3 than 4.0, that this pH is high enough to insure no appreciable reaction between iodide and arsenic acid, that the biphthalate plays practically no part in the adjustment

of the pH, and that it may be omitted without any material effect on the accuracy or precision of the method.

Reagents

The cupric sulfate solution was prepared from the salt which had been twice recrystallized from a solution of the c. p. pentahydrate, and was made 0.1152 *M* in copper sulfate. The concentration of this solution was determined electrolytically, and iodometrically by titration with thiosulfate solution which had been standardized against pure copper foil. Results by the two methods agreed within less than 0.2 per cent.

The sulfuric acid, ammonium hydroxide, potassium iodide, sodium thiosulfate, and potassium biphthalate consisted of c. p. reagents which conformed to the standards of Murray (2).

The iron and arsenic added as impurities were supplied from solutions of c. p. ferric nitrate and arsenic acid. These solutions contained approximately 0.1 gram each of iron and of arsenic in each cubic centimeter of reagent.

The ammonium bifluoride was Merck's Purified grade.

The starch solution was made from soluble starch prepared "according to Lintner."

Experimental Procedure and Results

Table I shows results of titrations of solutions of copper sulfate containing iron and arsenic as impurities. In series 1, 2, 4, 5, 7, 8, and 11 ammonium bifluoride, NH_4HF_2 , alone was used, and in series 3, 6, 9, and 10 potassium biphthalate was also present. The procedure was as follows:

To 25.00 cc. of copper sulfate solution containing 0.1831 gram of copper were added 5 cc. of a solution containing the impurities as designated in Table I and 5 cc. of concentrated sulfuric acid. This was followed by concentrated ammonium hydroxide until the blue copper complex began to appear. Then 6 *N* ammonium hydroxide was added dropwise until the solution smelled faintly of ammonia, and 2.0 grams of ammonium bifluoride and, in the runs indicated, 1.0 gram of potassium biphthalate were dissolved in the mixture. As soon as solution was complete, 10 cc. of 3 *M* potassium iodide were added and titration with thiosulfate was carried out. This procedure is essentially the same as that described by Park except in the cases in which the biphthalate was omitted. The amount of ammonium bifluoride added corresponded to 1 gram for each 0.1 gram of iron.

pH measurements were made by means of the quinhydrone electrode on separate solutions containing in 100 cc. (the approximate end-point volume) the same amounts of the same constituents that were present before the addition of the iodide. The iodide was omitted because it reduces the oxidized form of the quinhydrone and causes the pH determinations to be too high. Park in describing his procedure states that "the pH values of the solutions at the end point were determined by means of the quinhydrone electrode." If this means that potassium iodide was present, that condition alone might account for the fact that the authors' values are so much lower than his.

In the cases in which ammonium hydroxide was added until a faint odor was produced, the pH of the solution was approximately 3.3. In order to obtain a pH of 4.0 it was found necessary to add about 2 cc. of 6 *N* ammonium hydroxide more than that required to produce a faint odor of ammonia. This was introduced after the addition of the bifluoride. The quinhydrone potential was always read after the addition of the bifluoride. When the biphthalate was used, it was added after the bifluoride and its addition caused no recognizable change in the potential of the solution. In the cases in which the pH was 3.3, as well as those in which it was 4.0, the end points were sharp and after the titration was completed there was no further liberation of iodine for 15 minutes or more.

The values designated as "average per cent error" represent

the percentage differences between the iodometric titration on the blank (performed as described in the first paragraph under "Reagents") and the average of the titrations in question. The value of the blank was 25.37 cc.

TABLE I. EFFECT OF IMPURITIES ON TITRATION OF COPPER IN BUFFER SOLUTIONS OF AMMONIUM BIFLUORIDE WITH AND WITHOUT POTASSIUM BIPHthalATE

(Copper taken, 0.1831 gram. Volume of thiosulfate required, 25.37 cc.)

Series	Weight of Impurity		NH_4HF_2 Grams	$\text{KHC}_8\text{H}_4\text{O}_4$ Grams	Thio- sulfate Cc.	pH of Solution 2 cc. added to faint odor	
	Iron Gram	Arsenic Gram				NH_4OH added to faint odor	of 6 <i>N</i> NH_4OH added in excess
1	0.2	0.0	2.0	0.0	25.35	3.3	...
2	0.2	0.0	2.0	0.0	25.39	...	4.0
3	0.2	0.0	2.0	1.0	25.39	...	4.0
4	0.0	0.2	2.0	0.0	25.34	3.3	...
5	0.0	0.2	2.0	0.0	25.36	...	3.9
6	0.0	0.2	2.0	1.0	25.35	...	3.9
7	0.2	0.2	2.0	0.0	25.37	3.3	...
8	0.2	0.2	2.0	0.0	25.37	...	4.0
9	0.2	0.2	2.0	1.0	25.35	3.4	...
10	0.2	0.2	2.0	1.0	25.37	...	3.9
11	0.3	0.2	3.0	0.0	25.35	3.3	...

Average per cent error without biphthalate, -0.04; with biphthalate, -0.02. Average deviation of each result from mean without biphthalate, ± 0.06 per cent; with biphthalate, ± 0.06 per cent.

TABLE II. ANALYSIS OF A MIXTURE CONTAINING CUPRIC SULFIDE AND ARSENOPYRITE BY THE BIFLUORIDE METHOD

(Per cent of copper present, 14.72. Bifluoride added, 2.0 grams. Concentration of thiosulfate, 0.1022 *N*.)

Run	Weight of Sample	Volume of Thiosulfate	pH at End Point	Copper
	<i>Grams</i>	<i>Cc.</i>		<i>%</i>
1	1.097	24.86	3.3	14.73
2	1.241	28.15	3.3	14.74
3	0.9214	20.86	3.3	14.72
4	1.008	22.83	3.3	14.72
5	0.9210	20.88	3.3	14.73
6	1.051	23.77	3.3	14.70

Average percentage error, +0.01.

Average deviation of each result from mean, ± 0.07 per cent.

Table II shows results of analyses of a mixture containing approximately 22 per cent of c. p. cupric sulfide and 10 per cent of copper-free arsenopyrite mixed with finely ground unglazed porcelain which gave no test for iron when treated with hydrochloric and nitric acids. The cupric sulfide was thoroughly mixed with the unglazed porcelain powder and a number of samples accurately weighed out. Some of the samples were analyzed for copper and the values thus obtained were used as a basis on which to determine the error of the method. To each of the other samples was added about 0.1 gram of arsenopyrite, the whole thoroughly mixed, and the copper determined by the bifluoride method.

The procedure used on the blanks was essentially the same as that employed in the standardization of the thiosulfate by copper foil. Runs were also made on the blank samples, using the procedure described below for the mixture after the addition of the arsenopyrite. The two sets of values agreed within 0.1 per cent.

The procedure used on the cupric sulfide arsenopyrite mixture was as follows:

Fifteen cubic centimeters of concentrated nitric acid were added to the sample, evaporated to 5 cc., 10 cc. of concentrated hydrochloric acid and 10 cc. of 18 *N* sulfuric acid added, and the whole was evaporated to dense white fumes. In runs 1, 2, and 3, 10 cc. of concentrated nitric acid and 10 cc. of concentrated hydrochloric acid were then added, and the solution was again evaporated to dense white fumes and diluted with 20 cc. of water. In runs 4, 5, and 6 the fuming was followed by the addition of 20 cc. of water and 10 cc. of saturated bromine water, and the solution boiled until all bromine fumes were removed. These two types of procedure were found to be necessary to insure complete oxidation of the arsenic. After the addition of the water and boiling, the procedure was the same as in the titration

of the copper sulfate solutions previously described. In the present case it was not necessary to filter off the insoluble residue before making the copper titration.

Summary and Conclusions

In the Park method of determining copper in the presence of as much as 0.3 gram of iron and 0.2 gram of arsenic, the potassium biphthalate may be omitted without any appreciable effect on the accuracy or precision of the results.

The addition of biphthalate has no material effect on the pH of the solution.

The pH at the end point is nearer 3.3 than 4.0 and yet the end point is practically permanent.

To insure complete oxidation of an ore containing sulfide, iron, and arsenic, treatment with nitric acid alone is not sufficient. A double treatment with nitric and hydrochloric acids or a single treatment with the two acids followed by one with saturated bromine water is found necessary.

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The Determination of Rhenium

I. Qualitative

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SINCE the discovery of rhenium in 1925 (28) there have appeared a number of papers dealing wholly or in part with various qualitative tests for the identification of the element. Its place in the Noyes and Bray system was studied by Kao and Chang (16) who found that significant concentration was effected in the tellurium group. These authors reported that during the course of the analysis of the group, tellurium and rhodium could be precipitated in the presence of rhenium by reducing with hydrazine hydrochloride and sodium bisulfite in hydrochloric acid solution. Rhenium was subsequently precipitated as the sulfide from the filtrate.

The insolubility of rhenium heptasulfide was one of the characteristic properties early reported. Although this was a controversial subject for several years (14) it has been definitely established by several workers, notably Geilmann and Weibke (9), that the sulfide is quantitatively precipitated when a perrhenate solution containing as high as 33 per cent of hydrochloric acid by weight is treated with hydrogen sulfide. This separation is now used extensively in the analysis of rhenium. For reasons to be discussed below, the sulfide precipitation is not applicable to all rhenium-containing samples.

Although a number of papers have appeared dealing wholly or in part with reactions of rhenium of value in the qualitative detection of the element, no mention has been made of its place in the conventional scheme. Data are presented which indicate that in the Prescott and Johnson system the element will concentrate with arsenic. Early work in the field has been critically examined and evaluated and several new tests are reported. New confirmatory tests are described.

acid by weight it has been the author's experience as well as that of others (9) that precipitation is not quantitative. In light of this rather peculiar condition it was thought desirable to ascertain where in the conventional scheme of analysis the element would be concentrated and what precautions must be taken in order to insure a clean-cut separation.

A stock solution was prepared to which were added 5 mg. per 50 ml. of each of the following metals: Hg(ic), Pb, Cu, Cd, As(ous), As(ic), Sb, Sn(ic), Cr(ic), Fe(ic), Al, Ni, Co, Zn, Mn, Ca, Sr, Ba, Mg, K, and Na. Fifty-milliliter portions of this solution were carried through the qualitative scheme of Prescott and Johnson (19). Each group precipitate was washed thoroughly, digested with sodium hydroxide to expel all ammonia, oxidized with hydrogen peroxide, acidified with sulfuric acid, and treated with nitron acetate as described by Geilmann and Voigt (7).

In the case of solutions containing chromium and manganese it was necessary to add a few drops of alcohol to the acid solution prior to the nitron precipitation in order to reduce compounds of higher valence which yield precipitates with the reagent. Alcohol in low concentrations is without influence in the nitron precipitation (31). Certain normal constituents of complete group precipitates were excluded because it was found that they yielded insoluble nitron derivatives. For this reason tungstates, molybdates, palladium, gold, chloroplatinates, and germanium were not included in the stock solution.

A series of blank determinations using the stock solution was carried through the Prescott and Johnson separation and each group or subgroup analyzed according to the nitron method. No precipitate was obtained in any case. Fifty milligrams of rhenium as $KReO_4$ were then added to a 50-ml. portion of the stock solution and the separation and analysis repeated. Group I reagents yielded no precipitate. When hydrogen sulfide was passed into the 0.25 *N* hydrochloric acid solution for second group precipitation, some trouble was experienced in obtaining a flocculent precipitate. It filtered without difficulty, however, and was analyzed (30) for its rhenium content (first analysis, Table I).

The filtrate from the first precipitation with hydrogen sulfide was evaporated to a volume of 8 ml. for the arsenic precipitation. During the course of the concentration sulfur and rhenium sulfide separated from the solution. This was removed by filtration and analyzed for rhenium (second analysis, Table I). Samples 2, 3, and 4 were allowed to stand overnight before filtering.

The solutions were then acidified and saturated with hydrogen sulfide to precipitate the arsenic. The mixed sulfides were analyzed for rhenium (third analysis, Table I).

TABLE I. RHENIUM FOUND BY PRESCOTT AND JOHNSON SYSTEM

	(50 mg. of Re added)							
	Sample 1		Sample 2		Sample 3		Sample 4	
	Mg.	%	Mg.	%	Mg.	%	Mg.	%
First analysis	1.5	3.0	4.3	8.6	4.7	9.4	3.5	7.0
Second analysis	1.4	2.8	6.4	12.8	11.9	23.8	16.1	32.2
Third analysis	44.7	89.4	29.9	59.8	29.1	58.2	28.8	57.6
Total	47.6	95.2	40.6	81.2	45.7	91.4	48.4	96.8

Prescott and Johnson System

Although rhenium heptasulfide is quantitatively precipitated from solutions containing a relatively high concentration of hydrochloric acid, the precipitation takes place slowly. In solutions containing less than 4 per cent of hydrochloric

Analysis of group 3, precipitated in strict accord with the published procedure, yielded, in the case of the four samples, a barely perceptible precipitate of nitron perrhenate. Groups 4 and 5 likewise contained no rhenium. Colorimetric analysis of the sixth group indicated that the rhenium which had escaped precipitation in the second group had passed through with the alkali metals. Rhenium is normally precipitated completely with hydrogen sulfide from hydrochloric acid solutions of about the same concentration as those encountered in the precipitation of arsenic sulfide. The only apparent difference between the procedure followed in the Prescott and Johnson scheme and that followed in the routine quantitative analysis of rhenium products was that in the former case the solution was exposed to the action of hydrogen sulfide for but 5 minutes, whereas in the conventional Geilmann-Weibke precipitation the gas is passed through the solution for at least 1 hour.

Solutions were prepared containing 5 mg. per 50 ml. of the metals used in the previous separation and to these potassium perrhenate was added in varying amounts. The copper division sulfides were precipitated, quickly removed, and the filtrate was evaporated to 10 ml. The precipitate of sulfur and rhenium sulfide thrown out during concentration was not removed. Five milliliters of concentrated hydrochloric acid were added, the solution was warmed, and hydrogen sulfide passed in for 1 hour. The sulfide-sulfur precipitate was analyzed for rhenium.

TABLE II. TYPICAL RESULTS

Rhenium Added Mg.	Rhenium Found		Recovery %
	Copper division Mg.	Arsenic division Mg.	
7.0	0.0	6.9	99
11.0	0.1	11.0	101
16.0	0.1	16.0	101
25.0	0.4	24.7	100

Table II gives typical results obtained. It is apparent that heptavalent rhenium is concentrated in the arsenic group of the second division of the Prescott and Johnson system if a sufficient time is allowed for the precipitation of the sulfide. If the rhenium is present in the original sample in valence states lower than seven, the isolation not only will not be quantitative but in some cases most of the rhenium may pass into group 3.* Chlororhenous acid and rhenium trichloride, for instance, are unusually stable in solutions containing hydrochloric acid. It has been previously shown (4) that only a very small amount of rhenium as ReCl_6^{--} is precipitated by hydrogen sulfide. This, if present, would pass on into group 3 where it would be precipitated as hydrated ReO_2 when ammonia is added. Upon filtering and washing the group precipitate, oxidation takes place (6) and a portion of the rhenium passes on into group 4. The remainder will be oxidized to perrhenate when treated with sodium hydroxide and hydrogen peroxide, and passes through the aluminum, chromium, and iron separation without interfering with any of the confirmatory tests.

Any rhenium passing into group 4 as the result of oxidation during precipitation with ammonia or during the washing process will not be completely precipitated by hydrogen sulfide in ammoniacal solution. It is only by the long-continued passage of hydrogen sulfide into ammoniacal rhenium-containing solutions that appreciable amounts are precipitated (21).

Within the arsenic group large amounts of rhenium heptasulfide will not be dissolved when extraction is made with yellow ammonium sulfide. Rhenium if present in significant amounts may be detected in the residue by oxidizing a small portion with potassium hydroxide and hydrogen peroxide and observing the formation of characteristic rhombic bipyramides of potassium perrhenate. If desired, the sulfide may be brought into solution with sodium hydroxide and hydrogen peroxide and cesium chloride added to precipitate

cesium perrhenate. The latter reaction is somewhat more sensitive than the potassium perrhenate precipitation. Both are microscopic reactions in common use for the rapid identification of perrhenates. If large amounts of molybdenum and small amounts of rhenium are present, as in most mineral or industrial concentrates, the rhenium may be lost during the yellow ammonium sulfide extraction. Whether this is due to actual solubility or to colloidal dispersion is not known. The direct separation with 8-oxyquinoline (10), while excellent for moderate amounts of the two elements, is not applicable to small amounts of rhenium in the presence of large amounts of molybdenum because of adsorption of perrhenic acid on the voluminous molybdenum-8-oxyquinoline complex. If, for instance, the molybdenum-rhenium ratio be much in excess of 100 to 1 serious losses are encountered. The direct separation of the bulk of the molybdenum from rhenium is probably best accomplished by the distillation method of Geilmann and Weibke (8).

The small amount of molybdenum which normally distills with the rhenium does not interfere with the microscopic detection of rhenium as CsReO_4 or RbReO_4 . The large bulk of the distillate may be removed by slow evaporation without significant loss of rhenium. Although a great deal has been said about the volatility of perrhenic acid from hydrochloric acid solutions, the danger is not great if care is taken to have a small amount of fixed base present and if the evaporation is not carried out too rapidly or to dryness. This has been indicated by Kao and Chang (16) and has been the experience of several working in this laboratory. The following data are illustrative of this contention: Solutions containing 100 γ of rhenium as KReO_4 and 0.5 mg. of potassium chloride were diluted to 30 ml. with water and concentrated hydrochloric acid in the amounts indicated, and evaporated almost to dryness on a steam bath. Colorimetric analysis according to the method of Geilmann, Wrigge, and Weibke (12) was made upon the residual solution.

TABLE III. COLORIMETRIC ANALYSIS

Concentrated HCl	H ₂ O	Rhenium Found
Ml.	Ml.	γ
1.0	29.0	99
3.0	27.0	100
5.0	25.0	98
5.0	25.0	110
5.0	25.0	102
10.0	20.0	90
15.0	15.0	102
25.0	5.0	120
25.0	5.0	98

Evaporation of solutions of perrhenic acid with varying amounts of concentrated hydrochloric acid to a volume of about 0.5 ml. indicated upon analysis a loss of rhenium in some cases. One hundred gamma of rhenium was added in each case.

TABLE IV. COLORIMETRIC ANALYSIS

Concentrated HCl	Rhenium Found	Concentrated HCl	Rhenium Found
Ml.	γ	Ml.	γ
5	98	20	56
5	82	20	70
10	80	25	60
10	90	25	98
15	102	30	54
15	76	30	72

Noyes and Bray System

The place of rhenium in the Noyes and Bray (29) system has been studied by Kao and Chang (16), who found that the bulk of the rhenium recovered was with the tellurium-copper group and that concentration within the group was in the rhodium-iridium filtrate. The amount recovered was greatly increased by adding potassium chloride in the hydrochloric-

nitric acid evaporation (procedure 72) and by adding the washings from the ether extraction to the aqueous layer (procedure 73). The new procedure recommended involves the precipitation of tellurium and rhodium with hydrazine hydrochloride and sodium bisulfite from a hot hydrochloric acid solution. Any rhenium present passes into the filtrate where it is detected in the conventional microscopic manner.

Although this modification appears to be satisfactory when significant amounts of rhenium are present and when the exact procedure recommended by the authors is followed, the reduction with hydrazine in hydrochloric acid solution should be done with care and caution. Briscoe and collaborators (2), Noddack (24), Kraus and Steinfeld (17), and others have observed that hydrazine in acid solutions reduces rhenium to the tetravalent stage. As has been mentioned (4) hydrogen sulfide will not precipitate tetravalent rhenium from hydrochloric acid solutions. That hydrazine and hydrochloric acid are effective in the reduction of heptavalent rhenium is shown by the following experiments, performed during the course of an investigation of analytical methods proposed for the quantitative determination of the element (18).

Five milliliters of saturated solution of hydrazine sulfate, 5 ml. of concentrated hydrochloric acid, 32.2 mg. of rhenium as $KReO_4$, and 50 ml. of water were evaporated on a sand bath until a volume of 15 ml. had been reached. The solution at first turned yellow and later hydrated rhenium dioxide settled out. The acidity was reduced to above pH 5 by the cautious addition of sodium hydroxide and the resulting precipitate dried in a hot vacuum desiccator containing phosphorus pentoxide. On the assumption that the precipitate was rhenium dioxide, recoveries of 30.8, 34.0, 31.1, 34.1, 31.8, and 16.4 mg. were obtained. Although it was later shown by Geilmann and Hurd (5, 6) that any method involving the handling of rhenium dioxide is unreliable because of oxidation and adsorption errors, the results are significant in light of the proposed qualitative separation. Another series of nine determinations using ammonia in place of sodium hydroxide to induce hydrolysis yielded results ranging from 7.9 to 20.0 mg. out of 32.2 mg. added. In this case a large amount of colloidal dioxide remained in the solution. In light of these data care should be taken to observe the exact concentrations of reagents and time and temperature specifications of Kao and Chang (16) when following their proposed scheme.

Direct Detection

The direct separation and detection of rhenium in the presence of large amounts of molybdenum, iron, manganese, and other metallic constituents of minerals has received much attention. The first method proposed was that of Noddack (28) who presumably used alternate reduction and oxidation to isolate rhenium from minerals and mineral concentrates. The method in brief was to reduce large samples of the material under investigation or sulfide concentrates therefrom with hydrogen at about 900° C. Following reduction, the sample was heated in oxygen until no further sublimate appeared. The process was repeated several times and the sublimate from the entire process examined röntgenographically. Incidentally, element 43, to which the authors assigned the name Masurium, was said to have been isolated in the same manner. Although chemical methods were also used by the same authors (23, 26), their report on the analysis of 1600 minerals (26) does not indicate which of the minerals were directly concentrated by the sublimation method and which were concentrated by other means. Inasmuch as our knowledge of the distribution of rhenium is based upon these determinations and in light of the experience in this laboratory, the distinction is of some importance.

To the author's knowledge all rhenium compounds when heated to 900° C. in an atmosphere of hydrogen are reduced to the metal. When reheated in oxygen, metallic rhenium is converted to the volatile heptoxide, Re_2O_7 . In the presence of large amounts of basic oxides, however, the oxide immediately reacts with these to produce stable perrhenates. The vapor

pressure of most of these is relatively low even at the temperatures used by the Noddacks. Inasmuch as the richest rhenium-containing mineral yet reported has a rhenium content of the order of 2×10^{-5} , the preponderance of basic material makes the escape of appreciable amounts of rhenium heptoxide somewhat difficult. In the case of essentially acidic minerals the chance of isolating rhenium is much better than in basic materials. That fixed bases are effective in preventing the loss of rhenium when ignited in air has been discussed previously (14).

In a forthcoming communication from this laboratory it will be shown that certain minerals which contain rhenium in appreciable quantities yield no rhenium-containing sublimate when analyzed in accord with the direct oxidation-reduction method. Therefore for the qualitative detection of the element in minerals and concentrates the sublimation procedure is to be avoided unless it has been demonstrated that with artificial mixtures good recovery may be realized.

If the mineral is insoluble in hydrochloric or nitric acid it should be fused with sodium carbonate or with carbonate-nitrate mixtures. Prolonged digestion with nitric acid or with sulfuric acid should be avoided because of the danger of volatilizing perrhenic acid. Oxidizing materials of the type of pyrolusite may apparently be dissolved directly in hydrochloric acid without danger of losing rhenium. Table V shows the results of an experiment in which varying amounts of potassium permanganate or rhenium-free manganese dioxide were added to rhenium-containing solutions, hydrochloric acid was added, and the solutions were digested until decomposition was complete. Rhenium was then determined according to the sulfide-nitron method of Geilmann and Weibke (9). The errors are of the same magnitude as those obtained in the usual routine determination of rhenium according to the sulfide-nitron method.

TABLE V. DETECTING OF RHENIUM IN PRESENCE OF MANGANESE

Rhenium Taken	KMnO ₄ Added	Rhenium Found	Error
Mg.	Grams	Mg.	Mg.
28.8	1.0	28.3	-0.5
25.0	1.0	25.0	±0.0
28.8	2.0	28.7	-0.1
25.0	2.0	25.3	+0.3
30.2	3.0	29.3	-0.9
25.0	3.0	24.9	-0.1
28.8	4.0	28.4	-0.4
25.0	4.0	25.0	±0.0
25.0	5.0	24.9	-0.1
25.0	6.0	24.9	-0.1
25.0	7.0	24.8	-0.2
25.0	8.0	25.1	+0.1
MnO ₂ Added			
5.0	1.0	5.2	+0.2
5.0	2.0	4.9	-0.1
5.0	3.0	5.2	+0.2
5.8	4.0	5.9	+0.1
5.0	5.0	5.1	+0.1
6.5	6.0	6.7	+0.2
5.0	7.0	4.8	-0.2
4.5	8.0	4.1	-0.4

Either the hydrochloric acid solution of the carbonate-nitrate fusion or that resulting from direct acid decomposition of the ore may be adjusted for hydrochloric acid content (one-third by volume is recommended), heated to 90° C., and the rhenium precipitated with hydrogen sulfide. The sulfides may then be examined qualitatively for rhenium.

Spectroscopic Identification

According to Ida and Walter Noddack (22), if the rhenium content of a product is of the order of 10^{-6} the element may be detected by direct spectroscopic examination. As an illustration of this they cite the case of certain molybdenites having a rhenium content of from 10^{-5} to 10^{-6} in which they claim rhenium may be detected by direct resolution of the arc emission spectra.

The rhenium spectrum has been mapped by Meggers (20) who confirmed the early work of Noddack (27) regarding the wave length of the ultimate lines of the element. The three lines, known as the 3460 Å. triplet, have wave lengths of 3451.88 Å., 3460.47 Å., and 3463.72 Å. In addition there is a very strong line at 4889.15 Å. in the blue. Although more than 3000 spectral lines of the element are known, these four alone are of value to the analyst in the direct examination of rhenium-containing ores. The remainder drop out, under ordinary circumstances and with the usual equipment, when the amount of rhenium on the electrode is below 50 γ or 0.05 mg.

The spectrograph has been used extensively by the writer and his students in the direct examination of ores for the qualitative detection of rhenium. During the course of the work several instruments have been used—Hilger E₂ type Kruess single quartz prism with a low dispersion (10 Å. per mm. in the 3460 Å. region) but high intensity, a large Steinheil three-prism instrument of high dispersion in the 4889 Å. region and moderate intensity, a Bausch and Lomb constant-deviation spectrograph of low dispersion in the 4889 Å. region, but good intensity, and a large Bausch and Lomb instrument equipped with both quartz and glass optical systems. Both spark (20,000 volts) and arc (80 volts, direct current, 6 to 8 amperes) emission spectra have been studied. It is the conclusion of the writer that the direct spectrographic examination of minerals for rhenium is to be avoided and that a preliminary concentration should always be made. The reasons for this are several: In the first place no mineral is known which contains more than 2×10^{-5} rhenium. This in the author's experience automatically limits the lines available for study to the triplet and the 4889.15 Å. line in the visible region. All known rhenium-rich minerals have a very rich spectrum. Molybdenite, for instance, often contains appreciable amounts of iron in addition to the principal constituent, MoS₂. Columbite contains a wide variety of elements, many of which have a complex spectrum. Pyrolusite, a mineral which according to Noddack contains negligible amounts of element 75 but which according to Loring and Druce (14) contains considerable amounts, may contain from 1 to 5 per cent of iron with varying amounts of minor impurities in addition to manganese dioxide. When one considers that the rhenium content of no known mineral exceeds 2×10^{-5} it will be seen at once that a normal sample of ore placed on the end of an electrode represents at best but a few gamma of rhenium. This, coupled with the depressing effect which large amounts of other elements have upon the intensity of the rhenium spectrum, places it on the borderline of the sensitivity of our instruments. A further complication lies in the practical coincidence of lines of other elements with the four of rhenium. Iron, manganese, and molybdenum, for instance, have caused considerable trouble.

Whereas these elements would offer, for the most part, little interference in systems of high rhenium content, the exposures which the author has found necessary to bring out the rhenium lines in synthetic mixtures, when used on minerals, result in heavy broad lines which make positive identification of the rhenium spectrum somewhat doubtful.

Miscellaneous Qualitative Reactions

Perrhenic acid forms a large number of derivatives which have been proposed or used in qualitative identification. Of these, few are specific for rhenium. The microscopic precipitations of rubidium or cesium perrhenate as proposed by Geilmann and Brünger (3) are probably the most reliable and satisfactory. Care must be taken not to confuse the perrhenates with chlorostannates or chloroplatinates. The lower limit of sensitivity of the rubidium and cesium per-

renate reaction is given by the authors as 0.1 γ per 35 cu. mm. Tellurium, silver, and mercury perrhenate were found to have but limited application. Organic perrhenates investigated by the above authors and found to yield characteristic but not unique products were nitron, methylene blue, acriflavine, brucine, and strychnine. Nitron perrhenate precipitation has been utilized by Kronmann and Bibikowa (24) for the basis of a microchemical test. These authors allowed nitron acetate and sodium sulfide to react with a soluble perrhenate in a 10 per cent gelatin solution. When the mass had set, a drop of titanous chloride was added. Following the diffusion of this latter reagent into the gelatin a brownish yellow coloration around the nitron perrhenate crystals was to be seen. The reaction depends upon the relative speeds of the interaction of sodium sulfide, Re⁷, and Re⁴.

Although the reaction serves to distinguish between nitron nitrate and nitron perrhenate, it is not sensitive to much under 10 γ of rhenium and in such concentrations cesium or rubidium perrhenates are to be preferred. Heyne and Moers (13) prepared a veratrine derivative, the solubility of which indicated that it might serve as a micro reagent. During the course of a search for an organic reagent which would precipitate perrhenic acid but not chlororhenous acid (nitron yields an insoluble derivative with both), Scharf and Spiering (32) found that the following bases reacted with chlororhenous acid in concentrations of 5 γ per 25 cu. mm. but did not yield insoluble perrhenates in perrhenic acid solutions containing 30 γ per 25 cu. mm.: *m*-anisidine, *p*-anisidine, cinchonidine, tri-*n*-amyl amine, triisooamyl amine, dibenzyl amine, *o*-phenetidine, dimethyl-*o*-toluidine, methyl-*o*-toluidine, methyl-*m*-toluidine, dimethyl naphthyl amine, di-*n*-butyl aniline, di-*n*-amyl amine, diphenyl guanidine, 4-aminodiphenyl, and pararosanine. Safranine and antipyrine form insoluble perrhenates and chlororhenates. *N,N'*-Tetramethyl-*o*-tolidine (Tetron) has been established as a reagent for the gravimetric determination of chlororhenous acid in the presence of perrhenic acid (4) and may be also used to identify the former in the presence of the latter. Tougarinoff (33) reported that if an acid solution of perrhenic acid be treated with stannous chloride and potassium ferrocyanide a red color is produced. With dimethylglyoxime a yellow-colored complex is formed. The sensitivity of these reactions under optimum conditions is about 10 γ .

Röstrohr, Flame, and Bead Tests

The röstrohr technic described by Geilmann and Wrigge (11) will serve to detect and identify rhenium in concentrations of about 5 γ per 10 mg. and up. The metal is heated in the bend of a röstrohr of the conventional type until the condensation of rhenium heptoxide is complete. A small amount of sulfur is then introduced into the lower end of the tube and heated until it burns. The sulfur dioxide passing up the tube serves to reduce rhenium heptoxide previously deposited with the production of a blue oxide or compound of unknown composition. In some cases where the rhenium heptoxide ring is too light to be seen, the blue reduction product will be clearly visible. If molybdenum is present the sensitivity is decreased to somewhere in the neighborhood of 50 γ per 10 mg.

Care should be taken in interpreting negative results obtained as a result of the execution of this test. Rhenium as KReO₄, or as any other perrhenate stable at the temperature used, will not respond with positive results. Although the perrhenates may be reduced prior to the heating, unless the alkali be removed but a minor portion of the rhenium will be volatilized. If substantial amounts of alkali are present the rhenium will not be volatilized under any circumstances.

The rhenium flame is blue-green. It is not an intense color and, as has been pointed out (11), it is easily masked by other

elements. It is only in the oxidizing flame that the color is apparent.

Borax and phosphate bead tests yield with rhenium a gray color in a reducing flame. In the outer cone the color or turbidity, due to metallic rhenium, disappears as a result of oxidation.

Colorimetric Detection

The colorimetric determination of rhenium as developed by Geilmann, Wrigge, and Weibke (12) is by all odds the most convenient laboratory test available for the rapid detection of heptavalent rhenium. The Geilmann reaction is brought about by adding to a hydrochloric acid solution of a per-rhenate, stannous chloride and ammonium or potassium thiocyanate. A yellow-brown thiocyanate is produced which is soluble in ether, butyl acetate, and cyclohexanol. The complex is insoluble in carbon bisulfide, carbon tetrachloride, methyl cyclohexane, and aniline. Commercial malonic ester, methyl salicylate, resorcinol, benzyl alcohol, furfural aldehyde, and acetoacetic ester extract the color but for various reasons are not satisfactory. Although the reaction is subject to numerous influences which must be controlled before it is satisfactory as a quantitative determination (1), it is of great value as a qualitative test. The same reaction is, however, characteristic of molybdenum and unless this element is known to be absent the reaction cannot be considered specific. Although a number of extractors have been investigated in this laboratory, no water-insoluble substance has been found which does not extract both the rhenium and the molybdenum complexes about equally well. During the course of a study on the determination of rhenium in ores, minerals, and industrial concentrates (15) it was found that, whereas ethyl xanthate reacted with molybdic acid to yield a violet-red chloroform soluble complex, rhenium did not.

TABLE VI. DETECTION OF RHENIUM IN PRESENCE OF MOLYBDENUM

Rhenium Taken	Molybdenum Added	Apparent Rhenium Recovery	Error
γ	γ	γ	%
150	50	143	- 4.7
200	50	216	+ 8.0
200	80	216	+ 8.0
250	100	242	- 3.2
300	100	255	-15.0
60	100	64.7	+ 7.8
150	200	143	- 4.5
200	200	214	+ 7.0
200	300	210	+ 5.0
300	300	308	+ 2.7
60	300	55.2	- 8.0
250	400	273	+ 9.2
100	500	108	+ 8.0
150	1000	164	+ 9.3
150	1000	139	- 7.3
60	1000	57.1	- 4.8
100	1000	110	+10.0

It was found that if solutions containing molybdenum and rhenium were first treated with ethyl xanthate and the molybdenum complex was removed with chloroform, rhenium could be determined with fair accuracy in the remaining solution. Neither stannous chloride, hydrochloric acid, ammonium thiocyanate, nor mixtures of the three produced a color with residual traces of the xanthate. Although the accuracy of the method is such that it is not satisfactory without refinement for quantitative work, it serves rather well for qualitative detection. Table VI gives data illustrative of results which were obtained. Analysis for rhenium was made as described by Geilmann, Wrigge, and Weibke (12) after molybdenum had been extracted as a xanthic acid complex with chloroform.

The data presented were obtained while working on solutions free from metals other than molybdenum and rhenium.

Iron and copper are known to interfere. Oxidizing agents, excessive amounts of reducing agents, and high salt concentrations contribute to erratic results.

Phenyl hydrazine and thioglycolic acid both react with molybdenum but not with rhenium. Although like ethyl xanthate they are known to be unsatisfactory for the determination of molybdenum, an attempt was made to develop a satisfactory method which would allow the removal of the molybdenum so that rhenium could be determined in the residual solution. They were found to be unsatisfactory and inferior to ethyl xanthate.

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A Color Reaction for Detection of Cyclopentadiene

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SMALL quantities of cyclopentadiene can be detected as follows: One drop of the liquid to be tested is mixed with 1 cc. each of chloroform and glacial acetic acid and then treated cautiously with 2 or 3 drops of concentrated sulfuric acid. As little as 0.1 mg. of cyclopentadiene gives a distinct violet coloration.

Some higher boiling terpenes give a similar coloration but only with acetic anhydride, chloroform, and sulfuric acid.

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Potentiometric Determination of Mercaptans

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FROM the publications of various authors who have studied the methods of mercaptan determination, it may be concluded that a procedure based on the precipitation of silver mercaptides is the most reliable under conditions actually encountered in the analysis of petroleum products. The first such procedure, reported by Borgstrom and Reid (2), was a direct application of Volhard's determination of halides. In spite of some objectionable features which developed when applied to solutions of hydrocarbons, it has been considered by later workers the most reliable method in existence. Bond (1) used it with certain precautions to check the results of the copper oleate method. Malisoff and Marks (7) used the method in their work on thermal behavior of mercaptans. In the originally suggested form the procedure leads to the formation of emulsions, since aqueous silver nitrate is used for precipitation of mercaptans dissolved in hydrocarbons. The tendency of precipitated silver mercaptide to pass into the hydrocarbon phase, and to carry with it adsorbed silver nitrate, results in the necessity for a lengthy process of washing. An improvement of the method has been suggested recently by Malisoff and Anding (6), who found that the addition of methanol is beneficial, since the danger of formation of emulsions is minimized and the time of operation is shortened, there being no necessity for shaking and washing.

Outline of Proposed Method

The proposed procedure is based on precipitation of mercaptans with silver nitrate. By using enough alcohol to dissolve the sample and by titrating with an alcoholic solution of silver nitrate, the separation of phases, the formation of emulsions, and the resulting adsorption are completely eliminated. Furthermore, in order to avoid an excess of silver nitrate at the end of precipitation, the end point is determined potentiometrically with a silver electrode indicator. The method thus becomes applicable to colored solutions, as the selection of the end point is not dependent on a color change of the indicator. Finally, on account of the very low solubility of silver mercaptides, approximately equal to that of silver iodide, the method becomes applicable in the presence of substances which normally react with silver nitrate but form compounds more soluble than the silver mercaptides. The danger of the simultaneous precipitation of common impurities is thus minimized.

The influence of a number of substances likely to interfere with the suggested procedure was studied, especially those which occur naturally in petroleum products. Many were found to have no influence on the accuracy of the results, but hydrogen sulfide and elementary sulfur interfere with the procedure. Silver sulfide is considerably less soluble than the

A new procedure is described for the quantitative determination of mercaptans based on precipitation with silver nitrate. The titration is performed in an alcoholic solution of sodium acetate, using enough alcohol to dissolve the hydrocarbon sample, and titrating with a solution of silver nitrate in isopropyl alcohol. The end point is determined potentiometrically using a silver electrode as an indicator, thus avoiding an excess of silver nitrate and eliminating the danger of simultaneously precipitating impurities.

The method is applicable to colored solutions, as the selection of the end point is not dependent on a color change of an indicator.

silver mercaptides and is therefore precipitated from a mixture of sulfide and mercaptans before the precipitation of silver mercaptides commences. Theoretically, therefore, it should be possible to perform the determination of both hydrogen sulfide and mercaptans in one solution by titration with silver nitrate in one operation. This actually can be done for a certain limited range of concentrations. The procedure is now being studied, but cannot be recommended at present because its limitations are not yet known; it is suggested therefore that hydrogen sulfide be removed by washing the sample with acidified cadmium sulfate (10 percent cadmium sulfate, 2 per cent sulfuric acid, in water).

Elementary sulfur also interferes with the described procedure. Since the hydrocarbon sample to be titrated is added to a solution of sodium acetate in alcohol, and this solution is decidedly alkaline, a reaction between mercaptan and elementary sulfur takes place if both substances are present in the sample. Elementary sulfur should therefore be removed by shaking with mercury. This procedure does not alter the mercaptan content, as has been shown by Borgstrom and Reid (2).

A procedure which allows the estimation of elementary sulfur and mercaptans in one solution, based on the reaction between sulfur and mercaptans, will be described in a subsequent communication.

Apparatus and Experimental Procedure

A suitable simple arrangement for potentiometric titration of mercaptans is shown in Figure 1.

The cell consists of a silver half-cell sensitive to changes in silver-ion concentration and a mercury half-cell, *R*, used as the reference electrode. The silver half-cell consists of a silver electrode immersed in the beaker containing 50 cc. of 0.1 *N* sodium acetate in 96 per cent ethyl alcohol. The mercury half-cell and the bridge are filled with the same solution.

The silver electrode is a polished silver wire of about 2 mm. diameter, and the mercury electrode is a layer of mercury about 3 to 4 cm. in diameter. The cell is represented by the diagram



The e. m. f. of the cell is reasonably constant, about -0.070 volt, the minus sign signifying that the silver wire is the negative electrode. In the absence of any generally accepted standard reference electrode in alcoholic solutions, the mercury half-cell is used as the standard and the potential of the silver electrode is considered equal to the numerical value of the e. m. f. of the cell. Variations from this constant value may be caused by impurities on the silver wire. It is advisable to clean the electrode with a solution of potassium cyanide and then to wash it carefully with water.

On account of the somewhat high resistance of the cell, a reasonably sensitive potentiometer arrangement is required.

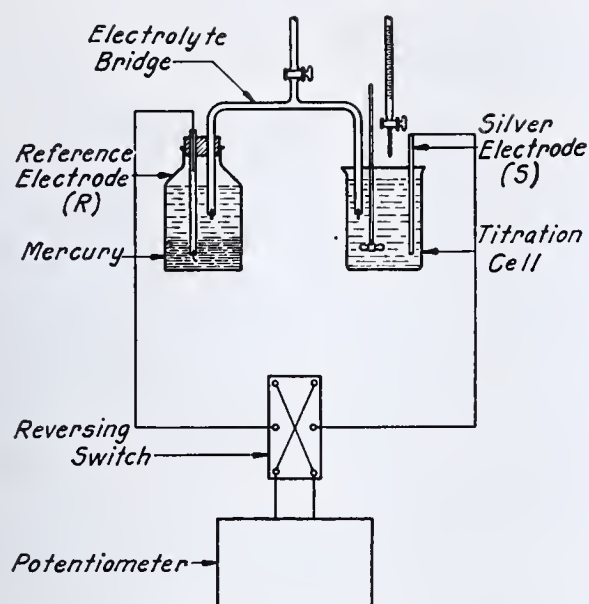


FIGURE 1. APPARATUS

The sample is added to 50 cc. of the alcoholic sodium acetate solution in the silver half-cell. The size of the sample may vary according to the solubility in alcohol of the solution examined and the amount of mercaptan present and should be such that about 10 to 15 cc. of 0.01 *N* silver nitrate solution are consumed. From 5 to 10 cc. of a hydrocarbon sample are usually soluble in the cell liquid.

If the sample (free from hydrogen sulfide and elementary sulfur) contains mercaptan, the potential of the silver electrode will rise from -0.070 to about -0.380 volt.

Standard 0.01 *N* solution of silver nitrate in isopropyl alcohol is added in small portions to the beaker with occasional stirring and the values of the e. m. f. of the cell are recorded. A sudden drop of the potential of the silver electrode to less negative values occurs at the end point.

SELECTION OF END POINT. If titration curves are constructed from the data observed they appear to be symmetrical, as would be expected, since the reaction involves two monovalent ions (5). The end point of titration is therefore at the point of inflection of the curve. If the results are not plotted the values of $\frac{\Delta E}{\Delta c}$ are calculated and the end point is taken where this value is a maximum. A typical titration curve is shown in Figure 2.

Reagents

SODIUM ACETATE IN ALCOHOL. Approximately 0.1 *N* solution of sodium acetate in 96 per cent ethyl alcohol is used as a medium for titration. Ethyl alcohol denatured with benzene or gasoline was found suitable.

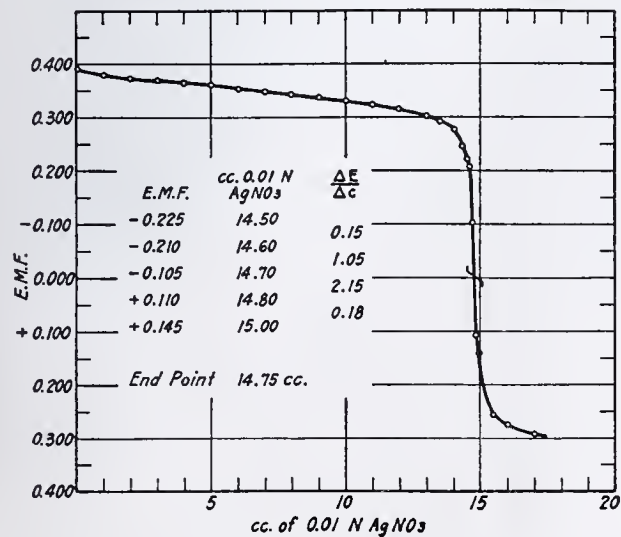


FIGURE 2. TITRATION OF *n*-BUTYL MERCAPTAN IN KEROSENE
5-cc. sample, 0.0295 *M*

STANDARD SOLUTION OF SILVER NITRATE. Solution of silver nitrate of 0.01 *N* strength in isopropyl alcohol containing about 9 per cent of water is prepared by exact dilution of a 0.1 *N* stock solution. The stock solution is stable for months but should preferably be kept in darkness. The dilute 0.01 *N* solution should be prepared as needed, but has been found to remain stable for several weeks. Ethyl alcohol is unsuitable for preparation of these solutions because acetaldehyde is slowly formed and fine silver powder is precipitated.

ISOPROPYL ALCOHOL. This must be free of aldehydic impurities. Commercial alcohol is purified by dissolving 0.5 gram of silver nitrate in 1 liter of alcohol, and exposing in a clear glass bottle to direct sunlight for several hours. The alcohol is decanted from the precipitated silver, the excess silver nitrate is removed with sodium chloride, and the alcohol is redistilled. The azeotropic mixture containing 9 per cent of water can be used directly for preparation of solutions of silver nitrate, as this amount of water aids in the solution of silver nitrate.

Interfering Substances and Conditions

INFLUENCE OF SOLVENT. The freedom of interference by the hydrocarbon solvent with the precipitation of silver mercaptides has been demonstrated by previous workers (1, 7). No disturbing influence of the solvent could be detected experimentally when titrations were performed in kerosene, cracked gasoline, amylene, acetone, and various aliphatic alcohols.

COMMON IMPURITIES. From a theoretical viewpoint substances reacting with silver nitrate and forming compounds substantially more soluble than silver mercaptides should not interfere with the procedure. Since the solubility of silver mercaptides is very low and nearly equal to the solubility of silver iodide, the chances of encountering an interfering substance are small.

The possible interference of a number of substances likely to be encountered in practice was studied experimentally. The procedure consisted in the titration of a solution of mercaptan of known strength, in the presence of a measured amount of substance examined for possible interference. Table I shows the results of analyses of *n*-butyl mercaptan solutions in kerosene containing varying amounts of diethyl disulfide.

TABLE I. TITRATION OF *n*-BUTYL MERCAPTAN IN PRESENCE OF DIETHYL DISULFIDE IN KEROSENE

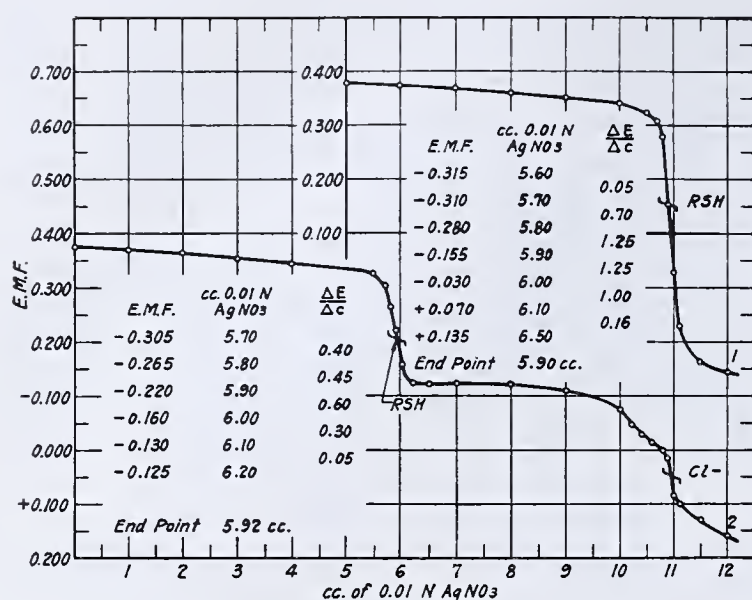
Diethyl Disulfide Present	Mercaptan Present	Mercaptan Found
Mole/l.	Mole/l.	Mole/l.
None	0.0297	0.0297
0.030	0.0297	0.0297
0.030	0.0297	0.0297
0.090	0.00425	0.00428

TABLE II. IMPURITIES NOT INFLUENCING RESULTS

Sulfur Compounds			
		%	%
Ethyl sulfide	0.1	Ethyl sulfone	0.1
Ethyl disulfide	0.1-0.2	Butyl sulfone	0.1
Carbon disulfide	0.2	Sodium cymene sulfonate	0.1
Thiophene	0.1-0.6	β-Trithioacetaldehyde	0.7
Reducing Substances			
Formaldehyde	0.04-0.40	Acetaldehyde	0.04-0.40
Miscellaneous			
Nitrobenzene	2.0	Phenol	0.1
Fuchsin	0.004	Pyridine	10
Sodium oleate	0.1	Light nitrogen bases ^a	0.4
Sodium sulfate	1.4	Medium nitrogen bases ^a	0.4
Magnesium sulfate	0.5	Heavy nitrogen bases ^a	0.4
Aluminum sulfate	0.5	Purified naphthenic acids ^a	0.4
Sodium bicarbonate	0.1	Crude naphthenic acids ^a	0.4

^a Separated from California crude oil.

By similar experiments it was found that certain substances had no influence on the results when present in the cell in the amounts shown in Table II.

FIGURE 3. TITRATION OF *n*-BUTYL MERCAPTAN IN ALCOHOL

1. In absence of chloride 2. In presence of chloride

Determinations were not influenced by the presence of chloride ion. The end point of mercaptan titration is reached long before the precipitation of the chloride ion begins. Figure 3 shows a titration of a solution of *n*-butyl mercaptan, with and without chloride added.

OXIDIZING SUBSTANCES, PEROXIDES. The determination of mercaptans in the presence of peroxides is often required, although this fact is not generally appreciated in the literature concerned with the determination of mercaptans in petroleum products. Occurrence of peroxides in gasolines is common and the oxidation of mercaptans may proceed very slowly when both substances are present in concentration often found in gasolines (8). The present procedure gives reliable results in the presence of reasonable amounts of hydrogen peroxide, ethyl ether peroxide, and organic peroxides formed in cracked gasoline when exposed to ultraviolet light.

In order to show that the proposed method is applicable in the presence of peroxides and because of the lack of any method to check the results of titrations in the presence of peroxides, the rates of oxidation of mercaptans were measured. Upon mixing a solution of *n*-butyl mercaptan with solutions of various peroxides, so that the resulting mixture was 0.01 *M* with respect to both components, and titrating immediately, no decrease in the amount of mercaptan took place. A change could be noticed only after several hours.

TABLE III. COMPOSITION OF MIXTURES

Solution	Solvent	Nature of Peroxide	Active Oxygen ^a Mole/l.
1	Ethyl alcohol	Hydrogen peroxide	0.01
2	Mixture 95% Ethyl alcohol 5% Ethyl ether	Ethyl ether peroxide	0.01
3	Mixture 50% Ethyl alcohol 50% Ethyl ether	Ethyl ether peroxide	0.1
4	Cracked gasoline	0.01
5	Mixture 95% Hexane 5% Ethyl ether	Ethyl ether peroxide	0.01

^a 0 = 16.

The results of several experiments in which the rates of oxidation were measured by potentiometric titration of mercaptans in presence of peroxides are shown in Figure 4. The regularity of the results suggests that the peroxides did not interfere with the determination of mercaptans. The curves represent the progress of oxidation of 0.01 *M* *n*-butyl mercaptan in various solvents by several peroxides. At the

start of the experiments the mixtures had the composition shown in Table III.

Influence of Concentration

A number of mercaptans purchased from Eastman Kodak Company were analyzed. A weighed amount was dissolved in kerosene and the solution was titrated at various dilutions. In all cases the end point was reached at, or near, -0.100 volt. This value was found experimentally to coincide nearly with the end point of the precipitation of silver iodide in the same solution, from which it is concluded that the solubility of silver mercaptides is approximately equal to (somewhat lower than) the solubility of silver iodide. The variations with individual mercaptans were too small to be considered for analytical purposes.

Table IV shows the influence of dilution on the analyses and gives an estimate of the absolute accuracy of the method.

TABLE IV. INFLUENCE OF DILUTION

Mercaptan	Present %	Found %	Purity of Sample %
Ethyl	0.3229	0.2706	83.8
	0.3229	0.2761	85.5
	0.0807	0.0684	84.7
	0.0202	0.0176	87.2
Isopropyl	0.3816	0.3220	84.4
	0.3816	0.3180	83.3
	0.3816	0.3160	82.8
	0.0954	0.0789	82.7
<i>n</i> -Butyl (1)	0.0239	0.0195	81.6
	0.4109	0.3895	94.9
	0.1027	0.0968	94.3
	0.0257	0.0243	94.6
<i>n</i> -Butyl (2)	0.2877	0.2681	93.2
	0.2877	0.2681	93.2
	0.2877	0.2681	93.2
	0.2677	0.2674	92.9
<i>n</i> -Butyl (3)	0.1041	0.0971	93.3
	0.01041	0.0097	93.2
	0.001041	0.0010	96.1
	0.3860	0.3680	95.4
Isobutyl	0.3860	0.3690	95.6
	0.0965	0.0924	95.8
	0.0242	0.0231	95.5
	0.4036	0.3945	97.8
<i>n</i> -Amyl	0.1009	0.0984	97.5
	0.0252	0.0246	97.6
	0.0252	0.0250	99.2
	0.4149	0.4110	99.1
<i>n</i> -Heptyl	0.4149	0.4110	99.1
	0.1037	0.1023	98.7
	0.0259	0.0258	99.6
	0.0259	0.0258	99.6
Benzyl	0.4002	0.3898	97.4
	0.4013	0.3377	84.2
	0.1004	0.0846	84.3
	0.0250	0.0206	82.4

ACCURACY. The principles on which the method is based and the freedom of interference by many impurities allow the conclusion that the absolute accuracy is high. The samples analyzed were not chemically pure preparations, and therefore the purity calculated from the analyses would be expected to remain below 100 per cent, as it actually did in all cases. In order to prove experimentally the absolute accuracy, pure mercaptans should be analyzed. An attempt was made to purify a sample of *n*-butyl mercaptan by fractionation in nitrogen atmosphere. The last fraction boiled at 98.0° to 98.3° C. (760 mm. of mercury), had a refractive index $n_D^{20} = 1.4425$, $n_D^{25} = 1.4392$, and analyzed by the Carius method 35.50 per cent of sulfur (calculated 35.57 per cent of sulfur). A weighed amount of this material was dissolved in kerosene, and a 10-cc. sample was titrated. The results of repeated analyses with checks are shown in Table V.

The potentiometric analysis indicated a purity of 93.3 per cent on the original sample before fractionation. The purified sample analyzed 97.6 per cent (average) by the potentiometric method, and 97.1 per cent by the iodometric method of Kimball, Kramer, and Reid (4). A comparison of the

physical properties of the purified sample with those given by Ellis and Reid (3) for a pure sample of *n*-butyl mercaptan which analyzed 100.3 per cent by the iodometric method, suggests that the authors' redistilled sample was still impure. Since the analysis for total sulfur by the Carius method indicated a purity of 99.8 per cent, the sample appears to have been contaminated by an inert sulfur compound.

TABLE V. ANALYSIS OF *n*-BUTYL MERCAPTAN PURIFIED BY FRACTIONATION

Weight of Sample	Concentration of Kerosene Solution	Found	Purity of Sample
Gram	Gram/100 cc.	Gram	%
0.1376	0.05504	0.1344	97.7
		0.1339	97.3
		0.1339	97.3
0.1183	0.04732	0.1157	97.8
		0.1152	97.7
0.1271	0.05084	0.1240	97.6
		Av. 97.57	

TABLE VI. PROPERTIES OF SAMPLE

	<i>n</i> -Butyl Mercaptan	
	Ellis and Reid	Sample purified by fractionation
Boiling point, ° C.	98.6-99.0 (768 mm. Hg)	98.0-98.3 (760 mm. Hg)
<i>n</i> _D ²⁵	1.4401	1.4392
Purity, %		
Iodometric method	100.3	97.1
Potentiometric method		97.6

PRECISION. The relative accuracy of individual determinations is governed by two factors—the solubility of the sample in alcohol and the amount of silver nitrate consumed per sample. The end point of titrations can be established with an accuracy of ±0.02 cc. This amount indicates 2 × 10⁻⁷ mole of mercaptan in the sample, which should be the error in the absolute amount of mercaptan found in the titration. Consequently, the precision shown in Table VII can be expected, if 10 cc. of sample are added to the cell.

TABLE VII. PRECISION

Molality of Sample	Mercaptan in Sample ^a	Calculated Error
	%	%
0.1	1.0	±0.02
0.01	0.1	±0.2
0.001	0.01	±2.0

^a Molecular weight = 100.

The experimental results of Tables IV to VI agree reasonably well within the calculated limits, considering that the extreme precision indicated by the calculations for the titra-

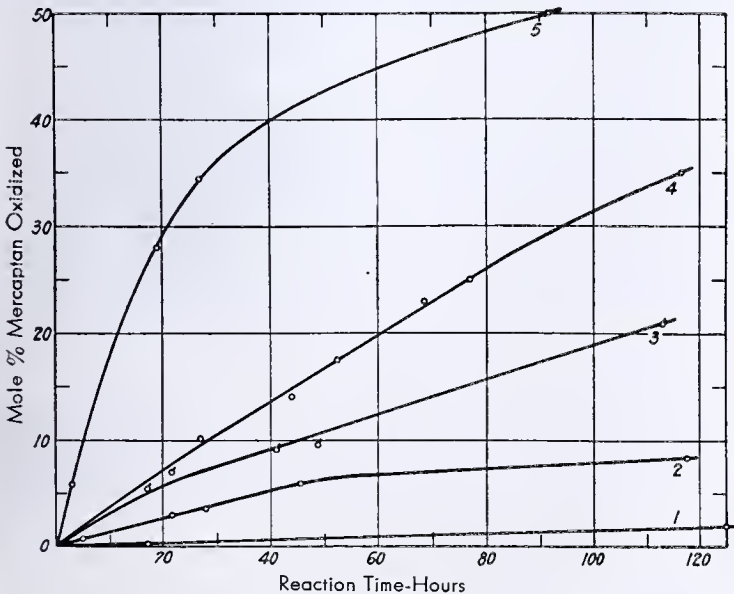


FIGURE 4. OXIDATION OF 0.01 M *n*-BUTYL MERCAPTAN BY PEROXIDES IN VARIOUS SOLVENTS

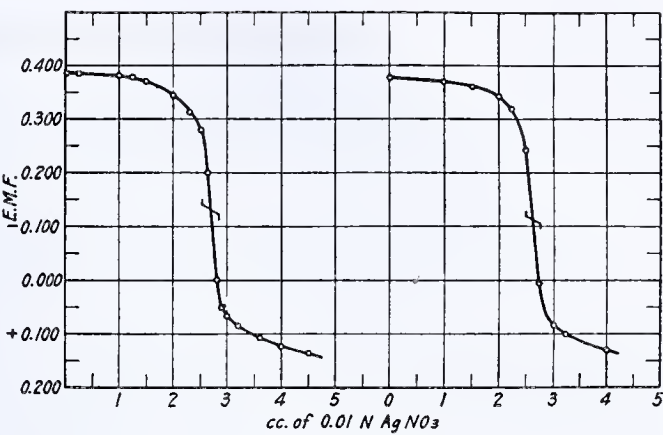


FIGURE 5. TITRATION OF MERCAPTANS IN A SAMPLE OF CRACKED GASOLINE FROM CALIFORNIA PETROLEUM

tion of more concentrated solutions could be verified only by observing special precautions. The somewhat erratic results obtained with ethyl mercaptan were probably due to its volatility.

Table VIII shows the reproducibility of mercaptan determinations in a sample of cracked gasoline from California crude; Figure 5 shows the reproducibility of the titration curves. Since solution was approximately 0.0025 M with respect to mercaptan, the expected error was ±0.2 × 4 = ±0.8 per cent. The maximum discrepancy found experimentally was about 2.0 per cent, an error of ±1.0 per cent, which is in reasonable agreement with the calculated value.

TABLE VIII. DETERMINATION OF MERCAPTANS IN CRACKED GASOLINE FROM CALIFORNIA CRUDE

Size of Sample	0.01 N AgNO ₃ Required	Mercaptan	Mercaptan Sulfur
Cc.	Cc.	Mole/l.	%
10.0	2.70	0.00270	0.0115
10.0	2.70	0.00270	0.0115
10.0	2.70	0.00270	0.0115
10.0	2.65	0.00265	0.0113

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IRON GALLATE INKS—LIQUID AND POWDER. A general study of iron gallate writing ink was undertaken at the National Bureau of Standards in an attempt to improve the keeping quality of ink without increasing the acid content. All inks of this type contain iron, and since the standard ink contains 3 grams of iron per liter, this figure was used as the starting point in devising the ink formulas. Experimental inks, using different materials in varying concentrations, were prepared and tested according to the Federal Specification. The use of gallic acid without tannic acid produced an ink with greater stability, and consequently the acid content could be decreased. This, in turn, decreased the corrosion of steel pens. The resulting ink had remarkably good stability. This modified formula could be adapted to the preparation of an ink powder without changing the characteristics of the ink.

Determination of Phosgene

In Gases from Experimental Fires Extinguished with Carbon Tetrachloride Fire-Extinguisher Liquid

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IN 1920, Fieldner and others (2) of the Bureau of Mines published the results of an investigation of the gases formed when excelsior fires are extinguished with carbon tetrachloride fire extinguisher liquid in a closed room. In 1931, Olsen (6) published a report which described the results obtained in a series of tests using the acetone method, the caustic soda method, and the aniline method for the determination of phosgene. In reporting the results obtained by the caustic soda method it was stated "as this method was used by Fieldner and his associates this source of error must have given high results in their experiments." The error referred to was the hydrolysis of carbon tetrachloride in the alkaline reagent and its subsequent titration as phosgene. Following publication of this article Matuszak (4, 5) called attention to the possibility of errors in Olsen's work which could equally explain the discrepancies found.

During 1933-34 the manufacturers of carbon tetrachloride-type fire extinguishers collaborated with the Bureau of Mines to check the results reported by Fieldner and others (2). This work was done by utilizing the same test chamber as that employed in 1920 and duplicating the test fires, conditions of burning, and test procedure as nearly as possible, except that the aniline method (1, 3), which is more specific for phosgene, was used. The results of this investigation are in substantial agreement with those reported by Fieldner and others (2).

Two sets of coöperative experiments were performed, the first at the bureau's Pittsburgh Experiment Station in the same chamber originally used in the 1920 tests, and the second in a gas laboratory previously used by Olsen and located at one of the manufacturer's plants at Newark, N. J. The representatives of the Bureau of Mines and of the manufacturers made separate determinations of phosgene during each series.

It must not be concluded that these tests with free-burning excelsior fires and heated iron in a small closed chamber show the quantities of phosgene which will be formed whenever and under whatever conditions carbon tetrachloride-type extinguishers are employed in extinguishing fires. The gases from fires are influenced by many factors, such as the kind and amount of burning materials, the condition of combustion, the moisture present, the absorption by materials with which they come in contact, and the size of the confining compartment or the lack of confinement. Attention is

This paper presents work done coöperatively by the Bureau of Mines and representative manufacturers of carbon tetrachloride-type fire extinguishers to check the values for phosgene reported by the Bureau of Mines in 1920 (2), which had been criticized (6) on the basis that the analytical method used gave results which were too high owing to hydrolysis of carbon tetrachloride in the alkaline reagent and subsequent titration as phosgene. This possibility of error was excluded in the present work by using the aniline method. The results obtained for phosgene are of essentially the same order and check the former work.

It is not the intention of this bureau to discourage the use of carbon tetrachloride-type fire extinguishers, which are excellent for stopping incipient fires, but rather to determine the decomposition products which may result from their use and which should be recognized and properly evaluated.

directed to these factors because it is undesirable to have erroneous conclusions drawn as to the usefulness and efficiency of fire extinguishers of this type, which enjoy a long, well-established record of effective service.

Experiments at Pittsburgh

EQUIPMENT AND PROCEDURE. The chamber employed at the Pittsburgh Experiment Station of the U. S. Bureau of Mines is the one used in the previous investigation (2).

The dimensions are $3.8 \times 3.05 \times 2.4$ meters. An air lock, $1 \times 1 \times 2.4$ meters, permits entering or leaving the chamber without much dilution of the chamber atmosphere. The total volume is approximately 28 cubic meters and exclusive of the air lock is 26 cubic meters. An opening in the ceiling is connected through a mercury-sealed bell-type valve to a suction fan which provides ventilation or removal of the chamber atmosphere when desired. A large circulating fan is located at one end and near the floor of the chamber. The ceiling is galvanized sheet metal, the walls are approximately half glass and half sheet metal, and the floor sheet metal is covered with linoleum. The metal surfaces have had many coats of paint and varnish in the course of their varied use. The exposed coating when the experiments discussed in this report were made was ordinary inside white paint. The fires were built on sheets of heavy transite board, supported in the center of the chamber 6.3 cm. above the floor by firebrick. A sheet of asbestos was suspended about 30 cm. below the ceiling area, directly above the fire to protect the chamber from the flames.

Excelsior was selected as the combustible material because the primary object of the work was to check the results of previous experiments (2) in which excelsior was used. In some of the tests the excelsior and the flames did not come in contact with any metals; in others, metal was present to a limited extent either as a galvanized-wire wastepaper basket in which the excelsior was placed, as steel barrel-hoop sections placed over the fire, or as iron wire supporting a bundle of excelsior 30 cm. (1 foot) above the floor.

The pile of excelsior was lighted at several points near the base and allowed to burn freely for 15 to 160 seconds with the chamber door open. The bell-valve in the ventilating duct was closed either before the fire was lighted or just before the extinguishing liquid was applied. When the fire had a good start the door was partly closed and the extinguisher fluid applied. The rate of application ordinarily was as rapid as possible to simulate the usual conditions of extinguishing a fire of the small size used in the experiments; in a few instances the application was slow, to prolong the duration of the small fires and thereby simulate con-

ditions of extinguishing fires larger than were permitted without damage to the test chamber. In certain cases the operator of the extinguisher was a representative of the Bureau of Mines and in others a representative of the manufacturers. Where the rate of extinguishing the fire was purposely delayed, it was manifestly necessary to protect the operator with a gas mask. In no instance did the representative of the manufacturers wear a mask. The extinguisher fluid was the preparation marketed by the manufacturers of carbon tetrachloride-type fire extinguishers and not ordinary commercial or c. p. carbon tetrachloride. It was applied to the fire with a standard 0.95-liter (1-quart) size hand-operated extinguisher. When the fire was extinguished the operator left the chamber and closed the doors, which made it gastight except for a 5-cm. (2-inch) hole in one side, left open to accommodate pressure differences created by cooling of the air, which otherwise would have collapsed the walls.

Tables I and II list the experimental conditions. In seven of the thirteen experiments the stirring fan was operated after the fire appeared to be extinguished. In experiments 2, 5, 9, and 10 (two with and two without the stirring fan in operation) the fire reignited, and it was necessary to enter the chamber three or four times and use the extinguisher.

TABLE I. EXPERIMENTAL CONDITIONS

(Application of carbon tetrachloride fire extinguisher fluid to excelsior fires and heated iron. Experiments at Pittsburgh.)

Experiment	Material Used for Experiment	Rate of Extinguishing	Stirring Fan Used	Loss in Weight of Excelsior Grams
1	1135 grams of excelsior placed on transite board on floor in center of chamber	Rapid	Yes	227
2	1135 grams of excelsior in wire basket on same board. Weight of basket, 500 grams	Slow	Yes	^a
3	1135 grams of excelsior in wire basket on same board. Weight of basket, 500 grams	Rapid	Yes	^a
4	1135 grams of excelsior in wire basket on same board. Weight of basket, 500 grams	Slow	Yes	^a
5	1135 grams of excelsior in wire basket on same board. Weight of basket, 500 grams	Rapid	Yes	136
6	1135 grams of excelsior placed on board	Rapid	Yes	^a
7	1135 grams of excelsior placed on board	Rapid	No	427
8	227 grams placed directly on board; control experiment, no extinguishing liquid used	None used	No	227
9	1135 grams in wire basket placed on board	Slow	No	^a
10	1135 grams of excelsior on board and 8 semicircular sections of sheet-iron barrel hoops placed over excelsior	Rapid	No	454
11	1135 grams of excelsior on board and 8 semicircular sections of sheet-iron barrel hoops placed over excelsior	Rapid	No	454
12	One end of 15-cm. I-beam weighing 8.7 kg. heated to red heat	Fluid applied slowly with dropping funnel	Yes	None used
13	1135 grams of excelsior suspended 1 meter above floor by baling wire from ceiling	Rapid	No	^a

^a Not determined.

METHOD OF SAMPLING AND ANALYSIS. The sampling of the atmosphere in the chamber was begun 3 to 5 minutes after the extinguishing fluid was applied to the fire. Two samples were taken simultaneously, each through a purifying tube—a 5-cm. glass U-tube with arms 22 and 30 cm. long. Figure 1 shows a purifying tube inside the chamber and a sampling train outside the chamber.

The short arm of the purifying tube contained 6 cm. of absorbent cotton at the top where the gas entered, and below the cotton 12 cm. of 10- to 12-mesh calcium chloride, previously neutralized with hydrogen chloride gas. The calcium chloride was not included until experiment 7. A small amount of cotton was placed in the connection between the two arms of the U. The long section of the purifying tube contained 10 cm. of amalgamated mossy tin at the bottom, then 3 cm. of mossy tin, and at the top 15 cm. of closely packed mossy zinc. Both purifying units were 1 meter above the floor and 10 cm. from the wall; unit 1 was at the midpoint of a long wall, and unit 2 was in the far corner of the adjacent wall.

Each sample was led through two simple absorption tubes of the petticoat bubbler type in series, each of which contained 25 cc. of the phosgene absorbent. The purifying train and connections to the absorption tubes were purged with the test atmosphere before the samples were taken.

Of the two samples taken simultaneously that taken through unit 1 was split into two parts, A and B in Table II. Each part was drawn through the purifying tube by means of a 20-liter aspirating bottle at a rate of 1 liter per minute. Sample C, taken through purifying unit 2, was started at the same time as samples A and B and was measured by a calibrated flowmeter. The sampling rate for sample C was 3.371 liters per minute for experiments 1 to 6, inclusive, and 3.268 liters per minute for experiments 7 to 13, inclusive.

The samples taken simultaneously in each of the first seven tests did not check, and it was thought that the discrepancies were due to variations in the chamber atmosphere at the two rather widely separated sampling points, particularly because each was near a wall where a minimum of mixing would be expected. Following experiment 7, the inlets to both purifying units were connected by 12-mm. glass tubing to a common sampling point 160 cm. above the floor at the center of the chamber. This sampling arrangement was used for the remainder of the experiments. The reaction of aniline in aqueous solution with phosgene (1, 3) to form *s*-diphenylurea, $\text{COCl}_2 + 4\text{C}_6\text{H}_5\text{NH}_2 = \text{CO}(\text{NHC}_6\text{H}_5)_2 + 2\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$, has been found (6) to give quantitative results for small amounts of phosgene in air.

In preparing the absorption solution an excess of aniline is kept in a bottle of distilled water for a week with occasional shaking, then phosgene is passed through the solution until a permanent precipitate of diphenylurea is formed and the mixture is kept ready for use. When a determination is to be made some of the solution is filtered several times through a Gooch crucible, and 25-cc. portions are placed in each of the bubblers. After the measured volume of sample is passed through the bubblers they are allowed to stand 2 hours, and the aniline reagent is then filtered through a weighed Gooch. Any precipitate which adheres to the sides of the bubblers is dissolved in warm alcohol and evaporated almost to dryness in a small beaker on a steam bath; several cubic centimeters of water are added and the evaporation is continued until there is no longer an odor of alcohol. This additional precipitate is then washed (with thorough policing) into the Gooch crucible and the entire precipitate is washed thoroughly with a solution of 1 *N* hydrochloric acid saturated with pure diphenylurea; the precipitate is then aerated several minutes and finally dried at 70° to 80° C. to constant weight.

The diphenylurea is extracted from the Gooch by washing with several portions of boiling ethyl alcohol, and the crucible is again dried at 70° to 80° C. to constant weight. The alcoholic extracts were dried in tared weighing bottles, first to dryness at room temperature, and then to constant weight at 70° to 80° C. These final weights were used in calculating the phosgene content of the gas.

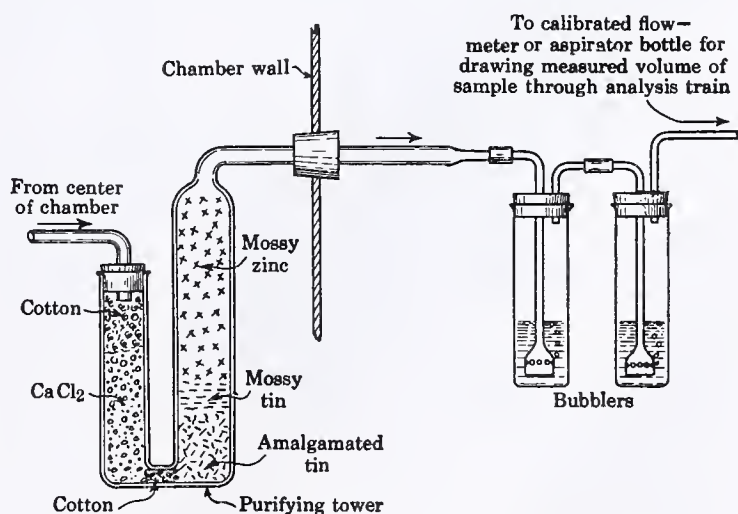


FIGURE 1. PURIFYING AND ANALYSIS TRAIN

TABLE II. DETERMINATIONS OF PHOSGENE

(In atmospheres created by application of carbon tetrachloride fire extinguisher fluid to excelsior fires and heated iron in 28-cubic meter chamber. Experiments at Pittsburgh)

Experiment number	1	2	3	4	5	6	7	8	9	10	11	12	13
Extinguisher fluid, grams	510	1880	540	940	900	630	625	None	1755	1545	980	790	1305
Number of times fire reignited	0	3	0	0	2	0	0	0	3	2	0	a	0
Number of applications of extinguisher fluid	1	3	1	1	3	1	1	0	3	3	1	1	1
Preliminary burning before application of extinguisher fluid, seconds	15	67	51	71	75	22	23	85	160	114	52	0	35
Total time of application of extinguisher fluid, seconds	20	168	15	81	22	8	14	0	198	54	33	420	70
Volume of sample, liters													
Sample A	18	18	18	18	18	18	18	18	18	18	18	18	18
Sample B	18	18	18	18	18	18	18	18	18	18	18	18	18
Sample C	62.4	60.7	60.7	60.7	57.3	60.7	58.8	58.8	58.8	58.8	58.8	32.7	58.8
Weight of diphenylurea found, mg.													
Sample A	0	31.6	25.1	15.0	10.7	10.8	2.7	0	11.9	5.8	5.1	21.0	2.8
Sample B	0	24.9	b	b	b	14.5	3.5	0	12.0	6.0	3.7	21.5	3.4
Sample C	2.1	47.3	4.8	9.5	5.0	9.6	6.8	0	32.1	14.9	8.8	33.3	6.6
Phosgene found, p. p. m. by volume													
Sample A	0	206	82	49	35	70	18	0	78	38	33	137	18
Sample B	0	162	b	b	b	95	23	0	78	39	24	140	22
Sample C	4	92	9	18	10	19	14	0	64	30	18	119	13

^a Hot iron beam, no fire.^b A and B combined for filtering and weighing.

At a room temperature of 23° C. and the usual barometric pressure at this location of 740 mm. of mercury, 1 mg. of diphenylurea is equivalent to 0.1175 cc. of phosgene. This value may be calculated in parts of phosgene per million parts of air by volume as follows:

$$1 \text{ mg. of diphenylurea} = \frac{0.1175 \times 1000}{\text{volume of sample in liters}} \text{ p. p. m.}$$

RESULTS OF INVESTIGATION. Table II gives the results obtained from the experiments at the Bureau of Mines. Three determinations (A, B, and C) were made during each experiment. In experiments 3, 4, and 5 figures appear for only samples A and C, sample B having been combined with A after precipitation of the diphenylurea.

In experiments 1 to 6, inclusive, the values for A and B do not check with sample C, which was of much greater volume. This discrepancy may be accounted for by the different method of treatment used on the precipitates from A and B compared with that used for sample C in these experiments.

The former were first treated with 0.5 to 1.0 cc. of concentrated hydrochloric acid, then after filtration the precipitates were washed with the filtrate containing aniline and undoubtedly some aniline hydrochloride and flushed with air to remove the aniline by vaporization. Sample C was washed thoroughly four or five times with 10 to 20 cc. of a 1 N solution of hydrochloric acid saturated with pure diphenylurea and filtered before use. The treatment used for sample C was also used for all samples from tests 7 to 13, inclusive. Its suitability had been checked previously by determination of known concentrations of pure phosgene in air and by washing known weights of pure diphenylurea in the same manner and drying again to constant weight.

It is possible that the treatment used for samples A and B in experiments 1 to 6 allowed varying amounts of aniline and aniline hydrochloride to be retained with the precipitate and calculated as phosgene, which accounts for the unusually high results found where it was used. The treatment used for sample C permitted more thorough washing of the precipitate without appreciable loss. The precipitates from experiments 1 to 6 were yellow-brown, probably owing to the presence of small amounts of tar or to oxidation during drying of the aniline or aniline hydrochloride retained in samples A and B, but in all cases sample C had definite crystals of diphenylurea which were easily recognized under the microscope. Virtually white precipitates were obtained after the calcium chloride had been placed in the purifying tube, and the more thorough method of washing was applied to all of the precipitates, experiments 7 to 13, inclusive. It was observed that the tar and smoke collected on the calcium chloride granules. In experiment 8, where no extinguisher fluid was used, no precipitate was obtained.

Another possible cause for differences in the results for samples A and B compared with C for tests 1 to 6, inclusive,

and also test 7, was variation in the composition of the chamber air at the two widely separated inlets to the sampling tubes; samples A and B were taken from one side of the chamber and sample C from a far corner. Figure 1 shows the connection to the common sampling tube to the center of the chamber that was used in tests 8 to 13, inclusive.

PURITY OF DIPHENYLUREA PRECIPITATES AND CONTROL EXPERIMENTS ON PROCEDURE. Melting point determinations were made on the precipitates obtained in several of the C samples, Table II. The results obtained were: Sample 2-C, 228° to 230° C.; sample 4-C, 228° to 231.5° C.; sample 10-C, 214° to 222° C.; sample 11-C, 228° to 230° C.; and sample 13-C, 233° C.

These melting points were obtained without any purification or recrystallization of the precipitate. A Thiele melting point tube and a Bureau of Standards calibrated thermometer were used.

The melting points of samples A were also determined, as follows: Sample 2-A, 183° to 190° C.; sample 3-A, soft at ordinary temperatures; sample 4-A, 181° C.; sample 5-A, 160° C.; sample 6-A, 164° C.; sample 9-A, 220° C.; sample 10-A, 210° C.; sample 11-A, 215° C.; and sample 12-A, 240° C. This indicates that the latter samples up to 6-A contained a much greater amount of impurity, which may therefore account for the high results found for these samples in Table II.

To obtain a sample of pure diphenylurea for a melting point determination the precipitates remaining from experiments 9-C, 10-C, 11-C, and 13-C, 47.3 mg. in all were taken up in 10 cc. of hot ethyl alcohol, evaporated to about half, then 10 cc. of water and 1 cc. of hydrochloric acid were added. Diphenylurea is fairly soluble in this mixture and sparingly soluble in water, but as the objective was only a purer specimen and not a quantitative yield, the mixture was filtered through a Whatman No. 42 paper and the precipitate washed thoroughly with water. It was then extracted with 20 cc. of hot absolute alcohol and evaporated slowly to dryness in a weighing dish and dried to constant weight at 60° C. A total of 19.6 mg. of crystals was obtained, which melted at 235.6°, 236.5°, and 236.5° C. in three determinations. The melting point given for diphenylurea in the International Critical Tables is 235° C.

For a control experiment 535 p. p. m. of hydrogen chloride and 356 p. p. m. of chlorine were put in the chamber and 110 liters were sampled at 11 liters per minute through two bubblers, each of which contained 25 cc. of aniline water. The gases were passed through the same purifying system that had been used for the samples of gases from the fires. No precipitate was formed. This indicated that these gases, which may be present in the gases from fires extinguished with carbon tetrachloride extinguishing liquid, did not interfere with the determination of phosgene by the method used.

When 23.2 p. p. m. of phosgene were added to this mixture of hydrogen chloride and chlorine in air and a 275.5-liter sample was taken at a rate of 11.02 liters per minute for 25 minutes, 19 mg. of diphenylurea, equivalent to 8.1 p. p. m. of phosgene, were found.

The chamber was ventilated, and 20.5 p. p. m. of phosgene were added from the cylinder, which had been thoroughly flushed out by allowing the gas in the cylinder to escape and be replaced by vaporization of the liquid. A sample taken for 25 minutes at a rate of 11.02 liters per minute yielded 47.2 mg. of diphenylurea, equivalent to 20.1 p. p. m. of phosgene.

Experiment 8 (Tables I and II) was duplicated, using 1135 grams of excelsior, which was ignited and allowed to burn for 30 seconds with no ventilation, then smothered with a large metal can. The heavy smoke was stirred and a 188.8-liter sample taken in 20 minutes through five parallel sets of two bubblers with 25 cc. of the aniline reagent in each. The samples were combined and filtered and treated the same as a regular phosgene determination. A small amount of black precipitate was obtained, which weighed 1.5 mg., but when calculated as phosgene on the assumption that the precipitate was diphenylurea it would be equivalent to only 0.93 p. p. m.

When 10 p. p. m. of phosgene were added to this same atmosphere, stirred for 5 minutes, and sampled and analyzed by the same procedure used in the previous experiment, 6.4 mg. of precipitate, equivalent to 4 p. p. m. of phosgene or 40 per cent of that added, were obtained.

A concentration of approximately 4000 p. p. m. of carbon tetrachloride vapor was made in a small chamber by evaporating a dish of the liquid on a hot-plate. Thirty-six liters of this gas were sampled through two bubblers in series containing 25 cc. of the aniline reagent in each at 2 liters per minute. No precipitate was observed in the reagent after standing for 2 hours. It was observed in other work that approximately 0.5 mg. of diphenylurea precipitate was readily visible in the solution.

A fire made by lighting 1135 grams of excelsior was allowed to burn 18 seconds with the chamber exhaust valve closed, and then was extinguished in 78 seconds with 973 grams of extinguisher liquid. A sample was started immediately and taken for 20 minutes at a rate of 9.44 liters per minute, total 188.8 liters, with the stirring fan on continuously. The final alcoholic extract of the diphenylurea was allowed to evaporate slowly and before it became dry 14.6 mg. of large crystals, needles 2 to 3 cm. long, were lifted out on a spatula. These had a melting point of 231.6° C. and represented 9.0 p. p. m. of phosgene. The remainder, upon drying, weighed 18.2 mg. and represented 11.3 p. p. m. of phosgene or a total of 20.3 p. p. m.

Experiments at Newark

A chamber was constructed early in 1934 in the plant of one of the manufacturers in Newark, N. J., to continue combustion researches previously carried out in a temporary structure. This chamber is similar in many respects to that at the Pittsburgh Experiment Station of the Bureau of Mines.

The dimensions are approximately 3 × 5 × 2 meters. The volume, including window bays and door frame, is approximately 32 cubic meters. The walls and floor are concrete, and the ceiling is transite asbestos board. It has five steel casement windows, 70 × 100 cm. (four opening to the outside and one to the laboratory) and a door in the end of the laboratory wall. The inside of the chamber had been given two heavy coats of sodium silicate and then brushed with dilute hydrochloric acid previous to its use for experiments with fires.

Experiments similar to those at the Bureau of Mines were conducted in this chamber, but no phosgene had been found when 18- to 36-liter samples were taken over a 36-minute sampling period. A very small amount of phosgene was found when iron sheets were suspended over the fire.

Since these results did not check those obtained at the Bureau of Mines the bureau agreed to send representatives to Newark for coöperative work to ascertain the cause of the apparent discrepancy.

METHOD OF SAMPLING AND ANALYSIS. The same analytical methods were used as in the Pittsburgh work, except for a few minor changes.

The purifying unit was slightly smaller, being one straight glass tube, 5.7 × 38 cm., with the inlet at the top. The sample passed through a 2.5-cm. layer of absorbent cotton, 7 cm. of "dessichlora," 10 cm. of 20-mesh zinc, 10 cm. of mercuric sulfide on 8- to 10-mesh pumice, and 5 cm. of 20-mesh zinc. For separating the precipitates of diphenylurea from the aniline reagent, Gooch crucibles with medium-fine sintered-glass disks were used

instead of the asbestos-mat type. These crucibles with the precipitates came to constant weight after drying at 70° C. for 2 hours. Large bubblers with 50 cc. of aniline water were used in sets of two in series for each sample. Eighteen- to 51-liter samples were taken through the phosgene absorbent with aspirator bottles, and larger 113- to 229-liter samples were taken by means of a suction pump and measured with a drymeter. The drymeter was checked against the aspirator bottles and found to agree within 2 per cent on a 36-liter sample. Corrections were applied to compensate for reduced pressure in the sampling system due to resistance of the purifying tower and bubblers. This did not exceed 40 cm. of water or a volume correction of about 4 per cent.

EXPERIMENTS WITH PURE PHOSGENE. Table III gives the results of experiments in which pure phosgene was admitted to the chamber for the purpose of checking the possibility of losing phosgene by reaction with the siliceous coating on the walls. The first section of Table III includes results of experiments made with the chamber in the condition in which it had been used previously for experiments with fires in which no phosgene was found. An old, very small purifying train, which had been used for experiments with fires, was included in the first two of these experiments; the second two sets of samples were taken directly from the chamber to the bubblers. The results for experiments 1, 3, 5, and 7 show no phosgene when 18-liter samples (the size used for experiments with fires in this chamber) were examined, although 5.67 to 22.9 p. p. m. of phosgene had been put into the chamber. With much larger samples (113 liters) the recovery was only from a trace to 11 per cent of the amount introduced. When 22.9 p. p. m. of phosgene were put into the chamber in the fourth of these experiments, not enough remained after a half hour to detect by odor, which indicates the amount present was less than 5.6 p. p. m. (Chemical Warfare Service, American University Experiment Station, Washington, D. C.)

TABLE III. EXPERIMENTS WITH PURE PHOSGENE INTRODUCED INTO CHAMBER AT NEWARK

Experi- ment	COCl ₂ Put into Chamber	Air Added with Gas	Sample Taken	Time of Sam- pling	Di- phenyl- urea	COCl ₂ Found	Recovery
	Cc.	P. p. m.	Liters	Liters	Min.	Mg.	P. p. m. %
1 ^a	250	5.67	b	18 113	36 33	0 Trace	0 Trace
3 ^a	750	22.5	b	18 113	36 30	0 1.6	0 1.6
5	750	22.9	19.8	18 113	36 30	0 1.8	0 1.8
7	750	22.9	16.1	18 113	36 36	0 2.4	0 2.5
Chamber Sprayed with Bakelite Lacquer							
8	750	22.9	31.0	18 113	36 29	2.7 8.6	17.3 8.8
9	3000	91.6	b	113	31	0	0
10	290	8.8	5.7	113	29	2.4	2.5
11	580	17.6	17.0	18 113	26 27	0 3.9	0 3.9
12	580	17.6	17.0	18 113	31 29	2.6 11.4	16.7 11.6
14	580	17.6	18.4	18 113	40 40	1.1 10.0	7.0 10.2
15	580	17.6	22.6	36 113	21.5 22	0 0	0 0
16	580	17.6	50.9	36 113	18 18	3.7 7.3	11.9 7.5
17	580	17.6	31.9	51 113	32 32	4.9 6.3	11.1 6.4

^a Analysis of phosgene used in experiments 1 and 3 gave a purity of 74.4 and 98.4 per cent. For the other experiments analysis showed a purity of 100 per cent. These values were used in calculating p. p. m.

^b Not determined.

^c The phosgene was allowed to remain in the chamber 2.5 hours to saturate the walls, after which the room was ventilated and a test was run which showed that no phosgene was present in the atmosphere.

^d With fire gases from smothered excelsior fire.

^e Stirring fan on only before sampling.

^f With fire gases and a freshly prepared purifying tower.

These experiments show that the chamber absorbed phosgene rapidly and provide an acceptable explanation for the failure to find phosgene in previous experiments with fires in this chamber. The rapid absorption very probably was due to adsorption by the silica gel formed on the walls by first coating them with sodium silicate and then treating with

dilute hydrochloric acid. Reaction with moisture on this kind of a surface would hasten removal of the phosgene. The cold concrete walls were continually wet from condensation of moisture from the atmosphere.

TABLE IV. DETERMINATION OF PURITY OF PHOSGENE USED IN NEWARK EXPERIMENTS

Experiment	Phosgene Used Cc.	Air Added for Dilution Liters	Temperature ° C.	Diphenylurea Mg.	Purity %
2	5.05	1	30	32.0	74.4
4	12.50	2	22	107.7	98.4
22	12.10	28	24	109.1	103.7

TABLE V. EXPERIMENTAL CONDITIONS FOR APPLICATION OF CARBON TETRACHLORIDE FIRE EXTINGUISHER FLUID TO EXCELSIOR FIRES

(Experiments at Newark. Material used, 1135 grams of excelsior placed on transite board on floor in center of chamber.)

Experiment	Rate of Extinguishing	Stirring Fan Used	Loss in Weight of Excelsior Grams
13	Rapid	No	^a
18	Rapid	No	303
19	Rapid	No	624
20	Slow	No	737
21	Slow	No	595

^a Not determined.

Following experiment 7 the chamber was cleaned and sprayed with two coats of a Bakelite-type varnish. After the varnish had dried overnight, further experiments were made on the reaction of phosgene with the chamber walls. In 6 experiments where 8.8 to 22.9 p. p. m. of phosgene were added, with and without fire gases present, the recovery was 22.0 to 94.0 per cent. However, in another experiment (No. 15) when a freshly prepared purifying tower was used and fire gases were present the recovery was zero after the addition of 17.6 p. p. m. The fire gases present in tests 11, 12, and 15 were produced by igniting 1135 grams of excelsior in the chamber and smothering with a large metal can.

Table IV gives the results of three experiments performed to determine the purity of the phosgene used in these tests. The phosgene was taken directly from the cylinder of compressed (liquefied) gas into a gas buret, using mercury as the confining liquid. The measured volume was then diluted with air and passed through aniline water, the analytical method used being the same as that described previously. The result found in experiment 2 (74.4 per cent) was low; therefore the valve was first opened to allow the gas above the liquid to escape and be displaced by freshly vaporized phosgene. When this precaution was taken the gas from the cylinder was found to be over 98 per cent pure phosgene. These results were used as a basis for calculating the amounts of phosgene added to the chamber.

RESULTS OF EXPERIMENTS WITH FIRES. When it was ascertained that after varnishing the surfaces about 50 per cent of the phosgene which was put into the chamber could be recovered in a 36-minute sampling period, five experiments with fires were made igniting 1135 grams of excelsior and extinguishing the fire with carbon tetrachloride fire extinguisher liquid, the experimental procedure being similar to that employed at Pittsburgh. Table V gives the conditions and Table VI the results of these experiments.

All the fires were made with the excelsior placed on a transite board platform 180 × 122 cm., placed near the center of the chamber and supported 7 cm. above the floor by tiles. A transite board shield of the same size was suspended 25 cm. below the ceiling to protect it and the ventilating valve. The excelsior was placed loosely on the transite boards and ignited around the edges, except in experiment 20, in which it was hollowed out and lighted under the pile.

The amount of phosgene found in these experiments ranged from 3.5 to 34.8 p. p. m. The precipitate from experiment 13, which showed 34.8 p. p. m., was not subjected to melting point or refractive-index tests. In this experiment the fire reignited and was allowed to burn during sampling until all the excelsior was consumed.

Large and small samples were taken in the Newark experiments, as in those conducted at Pittsburgh. One 56.6-liter sample was taken in experiment 13, but in each of the other four experiments with fires a small 36-liter sample and a large 176- to 229-liter sample were taken. This same arrangement was carried out in the experiments with pure phosgene in the chamber at Newark. The results from the larger samples are considered more reliable because the errors in weighing and from contamination of the precipitate with the aniline reagent or losses from solubility of the precipitate are smaller in proportion to the weight of the precipitate.

All precipitates from the 5 fire experiments reviewed in Table V were practically white; very little tar was observed, probably because the larger amount of fine material in the purifying tower was more effective in removing it. The melting points of the precipitates examined were much closer to the accepted value, 235° C., than those found in the Pittsburgh tests; in fact, several agreed closely with the melting points, 239° to 239.5° C., found for a specimen of Eastman Kodak Company's pure diphenylurea when determined under the same conditions with the same thermometer. A microscopic examination of the crystals for shape and refractive index also showed close agreement with crystals of the diphenylurea obtained from the Eastman Kodak Company.

TABLE VI. DETERMINATIONS OF PHOSGENE

(In atmospheres created by application of carbon tetrachloride fire extinguisher fluid to excelsior fires in a 32-cubic meter chamber. Experiments at Newark.)

Experiment number	13	18	19	20	21
Extinguisher fluid, grams	1308	991	936	960	1227
Number of times fire reignited.	1 ^a	0	0	0	0
Number of applications of extinguisher fluid	1	1	1	1	1
Preliminary burning before application of extinguisher fluid, seconds	30	47	32	25	25
Total time of application of extinguisher fluid, seconds	30	11	28	73	60
Volume of sample, liters					
Sample A	56.5	36	36	36	36
Sample B	...	229	199	205	176
Weight of diphenylurea found, mg.					
Sample A	17.0	1.9	3.9	7.0	6.0
Sample B	...	6.8	15.6	35.4	30.5
Phosgene found, p. p. m. by volume					
Sample A	34.8	6.1	12.5	22.5	19.3
Sample B	...	3.4	9.0	19.9	20.0

^a This fire reignited 4 minutes after it was extinguished and burned for 2 minutes during the sampling.

TABLE VII. MELTING-POINT DETERMINATIONS AND MICROSCOPIC EXAMINATIONS OF DIPHENYLUREA PRECIPITATES

(From experiments with fires extinguished with carbon tetrachloride fire extinguisher fluid at Newark.)

Sample	Melting Point ^a ° C.	Approximate Purity from Microscopic Examination %	Beta Index
13	^b		^b
18 A	221.5	80 to 90	1.62
B	235.5	75	1.62
19 A	232.5	80	1.62
B	235.5 to 237.5	80 to 90	1.62
20 A	229.5 to 235.5	90 to 100	1.62
B	238.5 to 239.5	95 to 100	1.62
21 A	229.5 to 234.5	90	1.62
B	235.5 to 238.5	90 to 100	1.62
Eastman Kodak Company's diphenylurea	239 to 239.5	100	1.62
Eastman Kodak Company's diphenylurea recrystallized from ethyl alcohol, dried at 70° C.	238.5 to 239.5	100	1.62

^a The thermometer used was compared with a Bureau of Standards calibrated thermometer, and the necessary corrections were made.

^b Not determined.

In all cases the beta index was 1.62. Table VII gives the melting points found for these precipitates and an estimate of the approximate purity of each precipitate as judged from its appearance under the microscope.

Absorption and Reaction of Phosgene

Attention is called to the importance of using materials for test chambers which absorb minimum amounts of phosgene, as this gas is highly reactive. Many contradictory results as to the formation and nonformation of phosgene, reported by different investigators engaged in work similar to that described in this paper, may be due to overlooking this important detail.

Summary

An article of comparatively recent publication (6) criticized the results previously reported by the Bureau of Mines in measuring phosgene in the gases from excelsior fires which were extinguished by carbon tetrachloride on the basis that the analytical method gave erroneously high values. This bureau, with the coöperation of the manufacturers of the carbon tetrachloride-type fire extinguisher, has repeated the investigation under a reproduction of the former conditions, except that a different analytical method was used. The phosgene found in these sixteen experiments in which excelsior fires were extinguished in a small sealed chamber ranged from 4 to 92 p. p. m. by volume, with an average of 23.6

p. p. m. When carbon tetrachloride was dropped on an I-beam previously heated to red heat and without fire present, the amount of phosgene found was 119 p. p. m. These results are in substantial agreement with those formerly reported by the Bureau of Mines. The report gives a detailed description of the experimental procedures and methods and a tabulation of the results obtained. The rapid reaction of the phosgene formed with other products of fire gases and with walls of the rooms in which the tests were made is pointed out and briefly discussed.

Acknowledgment

Acknowledgment is given with thanks to Alton Gabriel, associate chemist, Nonmetallic Minerals Experiment Station, U. S. Bureau of Mines, New Brunswick, N. J., for making the examinations of the diphenylurea crystals.

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Analyses and Softening Temperatures of Coal Ash

From Coals in the Northern Anthracite Field

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A REVIEW of the technical literature discloses very little information on the chemical composition of coal ash and its relation to fusibility and clinker formation from Pennsylvania anthracites, particularly for coals from the northern anthracite field. This paper has been written to supply data of this nature, to give a description of a method of minimizing clinkering troubles by means of draft control or the maintenance of oxidizing conditions in the fuel bed, and to illustrate a very simple method of estimating the ash-softening temperature from the chemical composition.

Table I contains analyses and softening temperatures of six samples of prepared anthracites, as marketed, selected from various localities in the northern anthracite field, and of two composite samples, made up by mixing a number of individual samples taken from different veins throughout the northern anthracite field. The ash-forming constituents of these coals consist mainly of high-fusing silica and alumina, with lesser amounts of the oxides of iron, calcium, magnesium, and the alkalis. The latter, with the exception of the oxides of iron, do not materially affect the softening temperature on account of their small quantities.

The copper shown in the analyses of two of these samples has been included because of its rarity in the ash of an anthracite and because of its possible effects as a catalyst in certain processes of coal treatment. The mineralogical constituents of coal ash as given by Marson and Cobb (4) are shown in Table II.

Draft Control to Minimize Clinker Formation

During the past 3 years the writers have carried out a number of experiments, both in the laboratory and on full-size combustion equipment, using anthracites from Pennsylvania, Wales, Scotland, Russia, and the Chinese Republic, and also coke and bituminous coal, for the purpose of obtaining further data on the causes of clinker formation and possible means of controlling it. The results of these investigations indicate that the ash-softening temperature of Pennsylvania's northern field anthracites, over the softening temperature

TABLE I. CHEMICAL ANALYSES AND SOFTENING TEMPERATURES OF COAL ASHES

(From various localities in northern anthracite field of Pennsylvania)								
Constituent	A	B	C	D	E	F	G	H
SiO ₂	55.00	55.70	56.62	55.10	56.08	55.04	55.4	56.5
Al ₂ O ₃	38.12	36.75	30.78	36.03	34.92	31.80	31.1	36.0
Fe ₂ O ₃	2.06	3.05	7.62	4.24	4.05	8.12	10.1	3.8
TiO ₂	1.82	1.32	1.10	1.52	0.96	1.22	1.8	1.2
CuO	0.09	0.04
MnO	0.03	0.08	0.10	0.05	0.10	0.12
CaO	1.20	1.40	1.10	0.91	1.40	1.30	0.3	0.8
MgO	0.60	0.62	0.72	0.68	0.84	0.76	0.0	0.3
Na ₂ O + K ₂ O	0.44	0.48	0.96	0.73	0.95	0.72	1.2	1.3
P ₂ O ₅	0.13	0.10	0.11	0.08	0.08	0.14
SO ₃	0.60	0.50	0.80	0.62	0.62	0.78	0.0	...
Softening temperature, ° F.	3000	3000	2925	2975	3000	2925	2660	2980

Samples A to F, inclusive, were analyzed in the laboratory of The Hudson Coal Company, and the ash-softening temperatures determined in the same laboratory by the A. S. T. M. method. Samples G and H were analyzed at the laboratory of the Anthracite Institute and the softening temperatures determined by E. P. Barrett at the Pennsylvania State College.

range ordinarily met with in commercial practice, is primarily dependent upon the content of iron compounds and to a lesser extent upon the content of the basis, lime, magnesia, and the alkalis.

TABLE II. MINERALOGICAL CONSTITUENTS OF COAL ASH

Element	Form
Silicon	Silicates and sand
Aluminum	Alumina in combination with silica
Iron	Small quantities of pyrite and marcasite, ferrous oxide, ferrous carbonate, ferrous sulfate, ferric oxide, ferric sulfate, "organic" iron, and iron silicates
Calcium	Carbonates, sulfates, silicates
Magnesium	Carbonates and silicates
Sodium and potassium	Silicates, carbonates, chlorides
Manganese	Carbonates and silicates
Sulfur (inorganic)	Small quantities of pyrite and marcasite, ferrous sulfate, and ferric sulfate
Phosphorus	Phosphates

Silica and alumina make up approximately 90 per cent of the ash from the northern field coals (Table I). Figure 1 (1) shows the melting points for the system silica-alumina. The silica-alumina ratios of the northern field anthracites fall on the small segment A, and it can be seen at once that such changes in the silica-alumina ratio as may ordinarily be expected in these coals will not greatly affect the softening temperature of the ash. Lowering of the ash-softening temperature below the range indicated at A is then necessarily due to the presence of the approximately 10 per cent of minor constituents, of which the compounds of iron form the major portion.

Fieldner, Hall, and Feild (2) have shown that coal ashes containing iron in the ferrous state soften at a lower temperature than when the iron is in the ferric state. For example, when pyrite, one of the important iron-bearing minerals found in the mineral matter of coal, burned under highly oxidizing conditions, the iron is oxidized to the basic oxide (Fe₂O₃) and when this combines with silica it forms high-melting compounds. If the atmosphere is partially reducing, the iron is oxidized to ferrous oxide (FeO) which forms low-melting compounds with silica. A still further reducing atmosphere will reduce the iron to the metallic state and thus has the effect of increasing the melting point toward that of the corresponding point on the silica-alumina curve by eliminating the oxides of iron and therefore their slagging effect. Proper regulation of draft and thickness of fuel bed will assist materially in overcoming or minimizing clinkering tendencies. Four practical rules for the accomplishment of this result in practice are given by Haslam and Russell (3).

1. Use thin fires and keep fuel bed level by placing fresh coal on thin spots. Disturb the fuel bed as little as possible.
2. Fire the coal in small charges to minimize crust formation.
3. Do not allow burning coal in the ash pit. It is a good plan

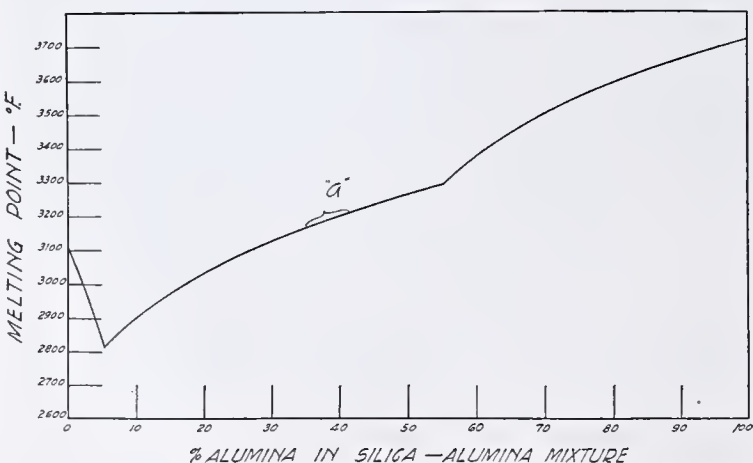


FIGURE 1

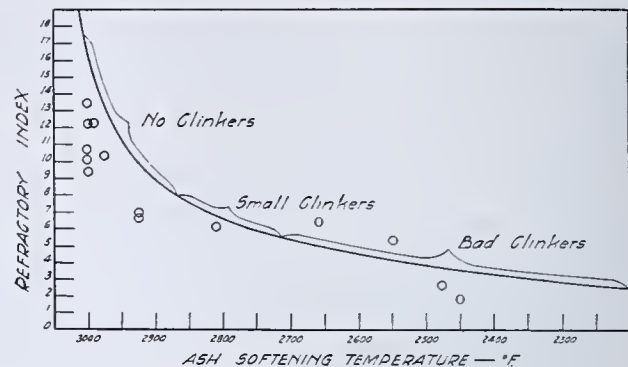


FIGURE 2

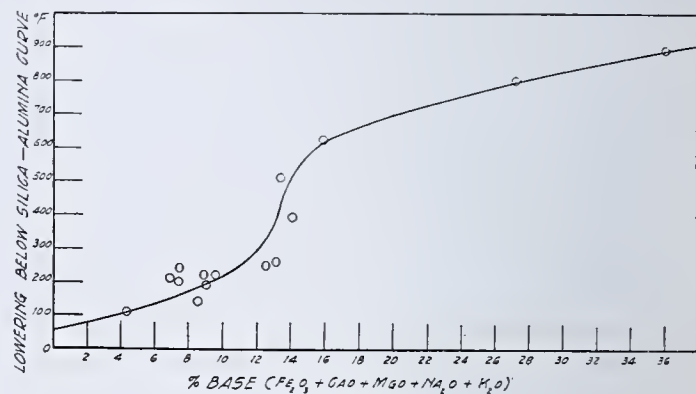


FIGURE 3

to keep water in the pit or, if it is not water-tight, to blow waste steam through the grate if the coal clinkers badly.

4. Keep the ash-pit door open and regulate the draft by means of the damper.

Prepared anthracite is practically free from extraneous pyrite, which is one reason for its high ash-softening temperature.

TABLE III. CHEMICAL ANALYSES, SOFTENING TEMPERATURES, AND CLINKERING CHARACTERISTICS OF ANTHRACITE COAL ASHES

	I	J	K	L	M	N	O
Duration of test, days	9.47	10.70	10.60	10.71	5.07	4.64	4.83
Draft, inches of water	0.029	0.028	0.029	0.030	0.029	0.027	0.028
Coal burned per hour, pounds	15.1	15.3	15.0	15.3	13.0	13.6	12.9
Rating developed, per cent	80.1	81.5	80.7	81.5	83.2	82.0	81.7
Clinkering	None	None	None	Small	Bad	Bad	Bad
Refractory index	21.0	9.4	10.7	6.1	2.7	5.3	1.8
Ash-softening temperature, °F.	3000	3000	3000	2810	2475	2550	2450
Chemical analysis of ash:							
SiO ₂	69.0	51.0	62.4	52.4	35.4	54.4	26.9
Al ₂ O ₃	26.5	39.4	29.1	33.5	38.2	29.7	36.9
Fe ₂ O ₃	3.2	9.6	5.7	10.9	19.3	9.9	28.9
CaO	0.4	..	0.3	2.0	5.8	6.0	4.4
MgO	0.2	..	0.3	0.6	1.5	..	1.3
Na ₂ O + K ₂ O	0.7	..	2.2	0.6	0.7	..	1.5

I, J, K, and L are Pennsylvania anthracites. M, N, and O are Welsh, Scotch, and Russian anthracites, respectively. Chestnut-size coals.

Refractory Index for Estimating Probability of Clinkering

Nicholls, Selvig, and Ricketts (5) show a fair relationship between the ratio

$$\frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}$$

and the softening temperatures of coal ashes. The results obtained by the writers are in agreement with this, as shown by Table III, which contains seven examples drawn from

fifty or more tests yielding similar data. Figure 2 shows a plot of the data given in this paper.

Estimation of Ash-Softening Temperature from Chemical Composition

A rapid but approximate estimation of the softening temperature of a coal ash or a mixture of coal ashes (as in blending) may be made from the chemical analysis of the ash as follows:

1. Determine the percentage of alumina on a basis of silica plus alumina equals 100.
2. From Figure 1 find the melting point of a silica-alumina mixture corresponding to the percentage of alumina found under 1 above.
3. Determine the percentage of basis (oxides of iron, calcium, magnesium, and the alkalies).

4. From Figure 3 determine the softening temperature lowering due to these bases.

5. From the figure found under item 2, subtract the lowering due to basis found under item 4 and obtain the softening temperature to be expected.

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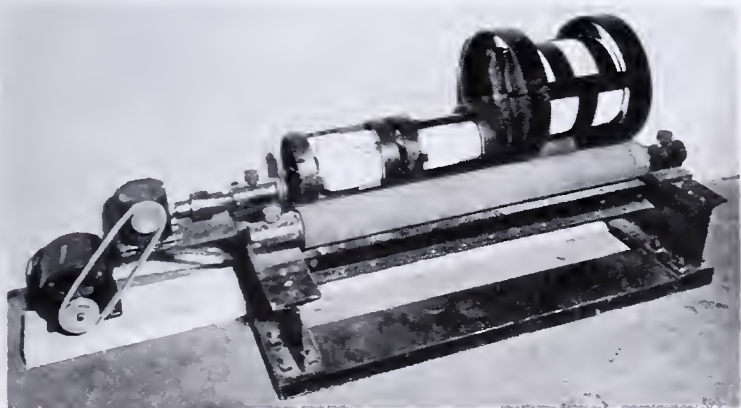
An Inexpensive Ball Mill

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IN SOME chemical laboratories a ball mill is a very useful and much needed piece of apparatus, although it may not be used as continuously as in a ceramics or other laboratory where large quantities of powdered materials are required. The most satisfactory ball mill in such laboratories should not occupy too much floor space, should be adaptable for use with ball mill jars or other containers of various sizes, and should be fairly inexpensive, simple, efficient, compact, and, if necessary, portable. The ball mill shown in the figure was designed and constructed to meet these requirements. A ball mill involving the same principle has been described by Furnstal (1).

The principle of the device is simple, there being two rollers on which cylindrical objects may be placed. The rollers are made from 90-cm. (3-foot) lengths of 7.5-cm. (3-inch) pipe, the ends of which are plugged. (Longer rolls can be used.) A piece of steel rod is inserted in the center of each plug to serve as the bearing axle. Ordinary brass bearing supports for holding the Babbitt metal, having a grease cup on top for lubrication, are used. The rear roller is connected through a speed reducer (20 to 1 ratio) and an ordinary V-belt to a motor, and is thus the "power" roller, while the front roller is free to rotate as it will. To increase the traction between the rollers and the racks for the jars and to quiet the operation of the mill, a piece of automobile inner tube is slipped over each roller. There is ordinarily sufficient traction between the objects and the rolls so that it is not necessary to connect the rollers by a belt. However, when small bottles about 5 cm. (2 inches) in diameter are used for preparing mixtures, traction is secured by placing a short length of pipe of about the same diameter on the rollers.

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In the figure, the support for the rollers is shown as pieces of I-beam, about 40 cm. (2 feet) long. If I-beam is not available, pieces of timber, railroad rail, or other material may be used. A series of holes is drilled in the upper surface of each I-beam. Each of the two bearings for the "idler" has two pins projecting from its lower surfaces. It is therefore possible to regulate the distance between the rollers by placing the pins in the proper set of holes, and to use containers of various sizes on the same machine. The rolls are close together when small jars are used; for larger jars, the distance between the rollers is increased.

The racks for holding the ball jars also can be made from inexpensive and easily obtainable materials. The rings for the racks are made from pipe of suitable diameter. For the small jars shown, 15-cm. (6-inch) pipe is used, and for the large ones, 30-cm. (12-inch) pipe. (The small jars hold about 1 liter, the large ones, 6.5 liters.) The rings for the large jars are attached to each other by two pieces of T-iron which also act as supports for the metal straps holding the jar in the rack. The rings for the small jars are held in place by strips of 1.3-cm. (0.5-inch) strap iron. One end of the small rack is partially closed by a cross of the strap iron. The jars are held in these small racks by a screw passing through a small bar of steel, which also holds the cover of the jar in place. When the bar is placed crosswise against one of the rings, the screw may be turned down against the cover of the jar, and the jar against the cross closing the other end of the rack, thus holding both the jar and the cover in their proper places.

Since for different sized containers there is an optimum speed for obtaining the best grinding results, this particular mill is driven by a direct current motor, the speed of which can be varied by a rheostat.

This particular set-up can also be used for producing uniform mixtures such as those used in ceramics, paints, etc. The materials can be put in a bottle or other suitable container and subjected to the rolling process in exactly the same manner as the ball mill jars are used.

The ball jars used for this mill were purchased from the Ceramics Department, University of Illinois. The actual construction of the machine was done by Arthur E. Wood, mechanic for the Chemistry Department, who also deserves credit for his many valuable suggestions. The cost of materials, which included three small and two large jars, was about forty-five dollars.

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RECEIVED November 16, 1935.

Determination of Viscosity of Small Samples of Oil from Oil-Impregnated Paper

Method and Apparatus

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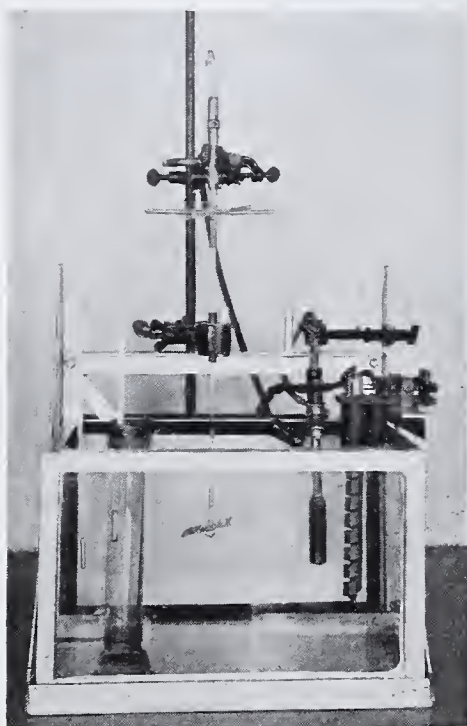


FIGURE 1. PHOTOGRAPH OF APPARATUS

difficult because only 0.5 to 2 ml. of the oil were available for test.

In the course of the investigations, several methods for determining the viscosity of small amounts of oil were tried. The first was the Ostwald method, which had to be abandoned because of the time involved in making the determination and the difficulty encountered in introducing the viscous oil into the apparatus. The second, which involved the use of a calibrated pipet, also proved unsatisfactory because of the difficulty of making suitable orifices adaptable over the wide range of the various cable oils tested.

A method using the ball and inclined tube type of viscometer has been found to eliminate these difficulties. Although the apparatus and method described herein may have numerous shortcomings, they have been used successfully. They are applicable to viscosity determinations on small samples, are fairly rapid, and lend themselves to ease of manipulation.

Description of Apparatus

The essential parts of the apparatus which is shown in Figures 1 and 2 consist of a capillary tube of approximately 2-ml. capacity for holding the oil to be tested and a small steel ball, the diameter of which is approximately one-half that of the capillary. During the development of the apparatus, it was found that when the capillary tube was placed directly in the thermostatically controlled water bath good checks could not be obtained. This was attributed to the fact that the bimetallic temperature-control mechanism which was readily available at that time was not sufficiently sensitive to control the temperature more closely than 0.28°C . (0.5°F .). The tube is held in position in a concentric glass

IT HAS been observed in the examination of the insulation of paper- and oil-insulated high-voltage cables taken from service that the viscosity of the oil in the insulation varies markedly from the center to the outside of the cable. This condition was also observed in cables subjected to laboratory treatments simulating service conditions. In order to interpret these changes, it was necessary to evaluate them numerically. This was

water jacket by means of rubber stoppers in such a manner that the capillary tube protrudes slightly through each end of the water jacket. By placing the concentric or "static" jacket around the capillary and then placing the jacketed tube in the water bath, a more nearly constant temperature could be obtained. The jacket also served to keep the tube nearer the desired temperature during the introduction of the oil into the tube. The temperature of the water surrounding the capillary tube is obtained by means of an A. S. T. M. viscometer thermometer (0.11°C ., 0.2°F . graduations) inserted in the upper rubber stopper. During the determinations this part of the apparatus is immersed in a thermostatically controlled water bath.

The capillary tube is scaled each 4 cm., so that the viscosity may be measured by the time necessary for the ball to pass between any two or more divisions, depending on the viscosity of the oil and the amount of oil available.

Manipulation of Apparatus

The manner of determining viscosity values is as follows:

With the capillary tube, *B*, open at both ends, the oil to be tested is poured slowly into it, care being taken to entrap no air. Because of the high viscosity of the oil it will not flow quickly into and through the tube, so that the lower stopper can be removed. When the tube is completely filled or when all the oil available has been added, a small cork is inserted into the lower end of the tube. The jacketed capillary tube assembly is then placed in a transparent walled water bath, maintained at a desired temperature (37.8°C ., 100°F ., in the case of the determinations mentioned herein), in such a manner that the capillary tube is held at an angle of 60° from horizontal.

The ball, which has been brought to the temperature of the oil, is quickly introduced through the top end of the capillary tube. The measure of the viscosity is determined from the length of time in seconds required for the ball to travel between selected graduations on the tube. Viscosity values are converted to the terms of a standard viscosity scale by means of factors obtained during the calibration of the instrument using oils of known viscosity. In observing the position of the ball care should be taken that the eye is always in the same horizontal plane with the ball and at right angles with the vertical plane of the tube, so as to avoid parallax.

Using a ball weighing 0.0548 gram and with a diameter of 0.237 cm. (0.0935 inch) and times of 8 to 300 seconds for a travel of 90 mm., it was found that the range of viscosities which could be covered was about 0.70 to 25 poise, which, for the oils under consideration, is equivalent to about 300 to 10,000 seconds, Saybolt Universal.

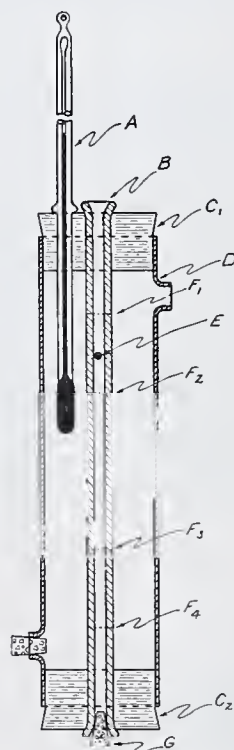


FIGURE 2. DIAGRAM OF ROLLING-BALL VISCOMETER

A. Thermometer, A. S. T. M.
B. Capillary tube
C₁, C₂. Rubber stoppers
D. Water jacket
E. Steel ball
F₁, F₂, F₃, F₄. Scale marks
G. Cork

Calibration of Apparatus

As it has been observed that oils extracted from aged cable sometimes exhibit viscosity values which vary over a wide range, it has been found necessary to calibrate the apparatus using several oils of known viscosity over a comparable range. The calibration consisted of a series of runs with the ball and

inclined tube viscometer using oils of known viscosities. The conversion factors obtained from these data are used in the calculation of the viscosity of the test samples.

This work forms a part of a general research program on the deterioration of high-tension underground cable being undertaken by The Detroit Edison Company.

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Determination of Water in Glycerol

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IF WATER is the only impurity in glycerol, it can be determined by specific gravity and reference to the tables of Bosart and Snoddy (2). However, all commercial glycerol contains other impurities which affect the specific gravity, so that an accurate value for water cannot be obtained in this way. A knowledge of the true water content is often required—for example, in the explosives industry to compare nitroglycerin yields on the basis of dry glycerol. Also, a direct determination is necessary in the complete analysis of crude glycerol. The international committee which adopted standard methods of glycerol analysis in 1910 (7) did not specify a method for the determination of water, indicating the unsatisfactory status of the methods available at that time.

Various methods depending on the measurement of physical properties have been described. Schmidt and Jones (10) and Kameyama and Semba (6) measured conductivity of electrolytes dissolved in glycerol. Grün and Wirth (3) used the determination of boiling point as an indication of water content. Hoyt (4) gave data on refractive index of glycerol containing various percentages of water. It is obvious that all these methods have the common defect of being accurate only for solutions of pure glycerol and water.

Berth (1) used boiling tetrachloroethane to remove water from glycerol, condensing the vapors and collecting the water in a graduated tube. Hoyt and Clark (5) used toluene for the same purpose. Lawrie (8) mentioned the use of calcium carbide to liberate acetylene equivalent to the water present. He also gave in detail the method of Rojahn (9) as modified by this laboratory.

The original Rojahn method consisted of distributing about 1 gram of the sample of glycerol on ignited asbestos in a special weighing bottle and exposing it to phosphorus pentoxide in a desiccator evacuated to 10 to 15 mm. After 12 hours under these conditions, the loss in weight was calculated as per cent moisture. The modifications developed here consisted of an improvement in design of the weighing bottle, substitution of fine glass wool for asbestos, and extension of the time of desiccation to 24 hours.

The modified Rojahn method has been used for a number of years as a standard procedure, but has not been entirely satisfactory. Duplicate determinations under the same conditions usually showed good agreement, but often did not agree with determinations by other laboratories on portions of the same sample. In some cases, an experienced analyst was unable to check his previous determination at a later date. Therefore, a further investigation was made with the object of learning the cause of these variations.

Preparation of Pure Glycerol

Dynamite glycerol was refluxed with a large volume of toluene for 16 hours, collecting the water in a Bidwell-Sterling type of moisture-receiving tube. A considerable amount of the water was removed in this way. The toluene was separated from the

glycerol in a separatory funnel, and the glycerol placed in a 3-liter distillation flask having a 25-cm. (10-inch) unpacked fractionating neck. It was then distilled slowly at about 5 mm. pressure and collected in a receiver which permitted fractionation without interrupting the distillation. The first 25 per cent of the distillate and a residue of about 15 per cent were discarded. Only the middle cut was retained. This distillation was repeated twice and a final middle cut was collected, without exposure to the air, in stoppered sample bottles, which were sealed with paraffin until used.

The determination of the specific gravity offers a convenient and reliable method for establishing the water content of pure glycerol (2). This method is recognized by the Committee on Glycerol Analysis and therefore has official status. Using it, the glycerol prepared as described above contained from 0.01 to 0.13 per cent of water. Considering the rapidity with which anhydrous glycerol absorbs moisture from the atmosphere and the necessary exposure in making a specific gravity determination, the purity and substantial freedom from water of the stock glycerol are well established.

In order to avoid absorption of moisture from the atmosphere, it was important that a technic for handling this essentially anhydrous glycerol should be developed. The following method was used:

The specific gravity was first determined in the usual manner in a Walker-type pycnometer. Upon completion, a one-hole rubber stopper was slipped around the outside of the neck of the pycnometer in an inverted position—that is, the large diameter of the stopper faced down. The capillary tube was now removed and the pycnometer quickly inverted over the mouth of a dry, tared Erlenmeyer flask, in which the inverted stopper fitted. As soon as the glycerol had been transferred, the pycnometer was removed and the flask carefully stoppered. Water and other impurities could now be added and their proportion determined by weight. The water found by the specific gravity determination on the purified glycerol was always included in the "calculated" water content of the sample. In order to remove samples for analysis, a Lunge pipet or a shortened 5-ml. pipet was used. In either case the pipet was introduced into the flask containing the glycerol through a rubber stopper, and filled by compressing a rubber suction bulb. In this way the glycerol was exposed to the atmosphere for a minimum of time, and no difficulty was experienced from this source.

Modified Rojahn Method

Portions of the specially purified glycerol, the water content of which had been established by specific gravity determinations, were made up to contain various percentages of water, such as are normally found in dynamite glycerol and crude glycerol. These were analyzed by the modified Rojahn method, as shown in Table I, which also includes similar determinations made in the presence of trimethylene glycol, a common impurity which is more volatile than glycerol.

The trimethylene glycol was prepared by distilling Eastman's practical grade at atmospheric pressure and collecting the fraction boiling at 212.6° to 214.5° C. This portion was redistilled once. It then contained 0.29 per cent of water (de-

Special attention should be given to the preparation of the U-tube, *T*. It should always be filled before the ground-glass surfaces are lubricated and these surfaces should be protected from particles of glass wool and dust from the desiccant with a cylinder of paper. The tube should be filled quickly with anhydrous magnesium perchlorate, after which a small wad of fine glass wool should be placed in each arm of the tube (cotton must not be substituted here). The ground-glass surfaces are best lubricated with "lubriseal." A piece of wire is used to suspend the tube on the balance. Before the U-tube is weighed, it is always wiped with a dry, clean cloth.

In preparing the sample tube, *R*, it is first fitted with a No. 8 rubber stopper, which has been drilled so that it can be placed around the outside of the tube in a position about midway of its length. A twist of copper wire, placed around the tube between this stopper and the side arm, serves as a convenient support for suspending the tube on the analytical balance. A wad of fine glass wool, about 40 to 50 mm. in depth, is packed in the bottom. The tube thus prepared is dried in an oven, preferably overnight, at 95° to 100° C. If a tube is needed on short notice, it may be dried in position in the apparatus at 100° C. and 2- to 3-mm. pressure for 15 minutes. When dry, the open end is closed with a rubber stopper and the side arm with a short piece of rubber tubing, plugged with a piece of glass rod. After being cooled to room temperature, the stopper should be raised momentarily in order to bring the pressure within the tube to normal. The tube thus prepared is weighed to the nearest milligram.

In taking a portion of a sample for analysis, it has been found useful to employ an ordinary 5-ml. pipet which has had both ends cut off at a point about 75 mm. from the bulb. The pipet is fitted with a one-hole rubber stopper of the size used for closing the end of the sample tube, *R*. This is placed against the lower side of the bulb of the pipet. The upper end of the pipet is closed with a 2-ml. medicine-dropper bulb, while to the lower end is attached a piece of glass tubing by means of a short piece of rubber tubing. The length of the glass tube may be varied according to the size of the bottle containing the sample. The sample is drawn into the pipet using a rubber suction bulb, after which the top is closed with the medicine-dropper bulb. The glass tube is then removed from the lower end of the pipet, which is carefully placed in the sample tube, *R*. It is then discharged by slowly compressing the medicine-dropper bulb several times, thus introducing a sample of 3 to 5 grams into the sample tube, prepared as above. Care must be taken not to deposit any glycerol on the side of the tube.

METHOD OF OPERATION. At the end of a determination, the apparatus is left completely assembled until the next analysis is made.

Assuming this to be the starting point and referring to Figure 1, stopcock *G* is closed, cocks *E*, *A*, and *B* are opened, and cock *C* is turned so as to connect tube *R* with U-tube *T*. The vacuum pump is then started and run 5 to 10 minutes. This serves to dry out the system after standing and to bring the U-tube, *T*, to the proper condition for weighing. This time may be employed in weighing the sample. To release the vacuum, close cocks *E* and *A*, stop vacuum pump, and open cock *G*; then turn cock *C* to allow air to enter the U-tube slowly through *H* and *J*; close cock *B*.

Place the dephlegmator, *D*, which has been dried in an oven, in the sample tube, *R*. Connect *R* to the weighed U-tube *T*, through the three-way stopcock, *C*, and put in place in the flask, *F*. Make water connections to dephlegmator *D*, and apply heat to flask *F*. Close stopcock *G*, open *E*, *A*, and *B*, and turn *C* to

connect *R* with *T*. Start the vacuum pump, and continue the dehydration for 45 minutes, accurately timed. Release the vacuum as described above. After turning *C* so that *R* is closed off, remove *T* and weigh to 0.1 mg. The drying cylinder, *H*, must be inspected occasionally to see that it is not clogged. If it is, the vacuum may not be completely released in the U-tube and weighings will be erratic.

Now restore the U-tube to the apparatus, close cock *G* and open *A*. Start the vacuum pump, turn *C* to connect sample tube *R* to U-tube *T*, then open cocks *B* and *E*. Continue the dehydration for 15 minutes, when the U-tube is again removed and weighed as before. At least two periods, 15 minutes in length, should be used to determine the completion of the dehydration and to estimate the gain due to leakage of the apparatus. The leakage gain should be constant within a few tenths of a milligram and be less than 1.5 mg. Constant leakage gains larger than this denote a need for renewal of the rubber somewhere in the system. Results are calculated as follows:

$$\frac{\left(W - \frac{TC}{15}\right) 100}{\text{Weight of sample}} = \text{Per cent moisture}$$

in which *W* = total weight gained by U-tube
T = total time elapsed in minutes
C = average correction due to leakage for a 15-minute period

The course of the dehydration is rapid for the first 30 to 45 minutes, at which time there is a sharp change in the rate of dehydration and from here on the gain is small but constant. That this is due to leakage and not to slow volatilization has been demonstrated by runs made with the sample tube empty. It is logical, therefore, that a leakage correction be made. It must, however, be determined for each run, as it varies slightly, depending on the tightness of the apparatus and atmospheric conditions.

TABLE III. ANALYSIS OF KNOWN SAMPLES BY VACUUM DISTILLATION METHOD

Water Present, %	Tri-methylene Glycol Present, %	Per Cent of Water Found					Deviation	
		1	2	3	4	Mean	From mean	From theory
0.02	..	0.02	0.04	0.03	0.01	+0.01
0.06	..	0.03	0.05	0.04	..	0.04	0.01	-0.02
0.05	..	0.03	0.05	0.04	0.01	-0.01
0.68	..	0.72	0.68	0.69	..	0.70	0.02	+0.02
1.10	..	1.06	1.11	1.10	..	1.09	0.03	-0.01
1.49	..	1.51	1.46	1.51	1.47	1.49	0.03	0
4.93	..	4.83	4.90	4.83	..	4.85	0.05	-0.08
0.06	1.19	0.04	0.05	0.04	..	0.04	0.01	-0.02
1.19	1.18	1.23	1.23	..	+0.04
1.10	1.15	1.14	1.14	1.10	1.14	1.13	0.03	+0.03
1.14	0.97	1.08	1.15	1.11	..	1.11	0.04	-0.03
4.85	4.65	4.90	4.84	4.94	4.86	4.89	0.05	+0.04

While the first determination is in progress, the sample for the next may be prepared or other work carried on. When the determination is complete, the water is turned off the dephlegmator and the water inlet tube removed first. This allows the water to siphon out of the dephlegmator, and prevents flooding of the apparatus.

The above procedure is given in considerable detail, but with a little experience it will be found simple and convenient. A determination may be completed in 2 hours or less. The attention of the analyst is required during only a part of this time so that other work can be carried on simultaneously.

DATA. The same glycerol was used to prepare known samples as in the study of the modified Rojahn method. Trimethylene glycol, also prepared as above, was added to several samples to demonstrate that it does not interfere. The results obtained are shown in Table III.

The data on known samples show that the vacuum distillation method is precise and accurate for determination of water in pure glycerol and in glycerol containing trimethylene glycol. The relative error is not greater than 3 per cent in samples containing normal amounts of water. With ordinary care there is no difficulty in getting the agreement on duplicates shown in Table III. A limited number of check analy-

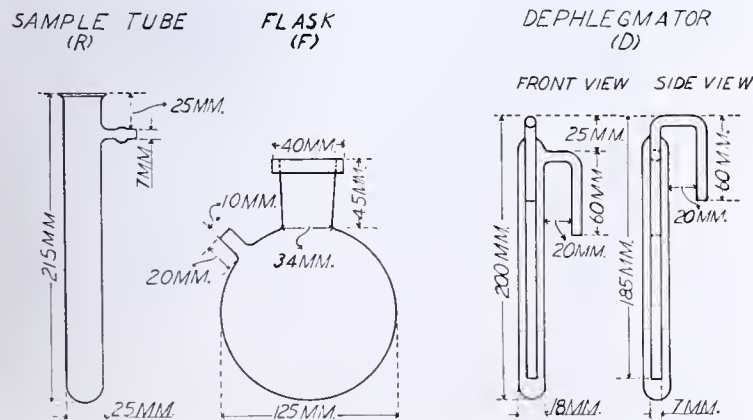


FIGURE 2. DETAIL OF SAMPLE TUBE, FLASK, AND DEPHLEGMATOR

ses by other laboratories have shown excellent agreement, which is gratifying in view of the fact that they had no previous experience with the method.

In Table IV are shown typical results obtained on analysis of commercial crude and dynamite grades of glycerol in comparison with similar analyses by the modified Rojahn method.

TABLE IV. DETERMINATION OF WATER IN COMMERCIAL GLYCEROL

Sample	(Comparison of the new method with the Rojahn method)					
	Per Cent of Water Found			Desiccation over P_2O_5 for:		
	Vacuum distillation	24	48	24	48	72
	1	2	Av.	hours	hours	hours
Dynamite No. 1	0.44	0.45	0.45	0.75	0.81	0.90
Dynamite No. 2	0.73	0.74	0.74	0.82	0.93	1.04
Crude No. 1	5.79	5.77	5.78	5.57	5.92	5.92
Crude No. 2	4.41	4.43	4.42	3.89	4.52	4.77

This is further evidence that the desiccation over P_2O_5 is unreliable. One of the dynamite glycerols showed fairly good agreement with the new method in 24 hours, while the other gave a result almost 70 per cent too high. In the crudes both were somewhat low at 24 hours and gave more nearly correct values at 48 hours. The longer time required appears to be caused by the formation of a layer of phosphoric acid over the surface of the phosphoric anhydride, thus reducing its efficiency as a desiccant. Over activated alumina, a desiccant which is granular and porous but admittedly of lower efficiency than P_2O_5 , a value of 4.50 per cent of water was obtained on crude No. 2 in 24 hours.

Precaution

Anhydrous magnesium perchlorate should be classed as a potentially dangerous chemical, just as are sulfuric acid, metallic sodium, etc. Accidents have resulted from the accidental admixture of sulfuric acid with this compound to form perchloric acid, which, in turn, exploded in contact with organic matter. In view of this, the following precautions must be followed:

1. Never use sulfuric acid to replace potassium hydroxide in drying tower H.
2. The chemical should be kept free from organic material as far as possible. Never use a cotton plug to replace glass wool in the U-tube.
3. The chemical should be handled and the spent material disposed of only by the chemist, and never should be left to a janitor or clean-up boy.
4. The spent chemical should not be thrown into waste jars or sinks. It should be dissolved in water and disposed of in a drain, ditch, or other safe place outside the laboratory.

Where these precautions are observed, there should be no trouble resulting from the use of anhydrous magnesium perchlorate as a desiccant.

Summary

A critical study has been made of the modified Rojahn method, showing that it only approximates the true water content. It gives varying results due to inadequate control of the following factors: (1) the temperature of the room as it affects the volatility of glycerol at the reduced pressure; (2) the presence of varying amounts of volatile impurities other than water; and (3) the loss of efficiency of the desiccant when comparatively large quantities of water are present, as in crude glycerol.

A new method, designated the vacuum distillation method, is described. It is based on the removal of water from glycerol at 100°C . and 2- to 3-mm. pressure. The volatility of the glycerol and low-boiling impurities in glycerol is controlled by a reflux condenser, which separates these ingredients from

the water vapor. The water vapor is absorbed in a desiccant and weighed.

The vacuum distillation method is shown to give the true water content of glycerol with a relative error of not over 3 per cent on samples containing 0.5 to 5 per cent of water. Results are readily duplicated and are available in a maximum time of 2 hours. The attention of the chemist is required during only a fraction of this time. The method is applicable to crude and refined glycerol.

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Calculating the Blank

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MANY volumetric determinations require an excess of the reacting solution to produce a visible end point. For accurate work this excess must be subtracted from the total amount added in order to obtain the correct titer. The magnitude of this excess may be determined directly by titrating a blank, on which the end point is apt to be uncertain, or it may be calculated in the following manner.

If two or more samples of different weights are run under exactly the same conditions, the amount of excess reagent should be the same in each case and simple equations may be used to calculate it.

Example

A zinc solution was titrated with ferrocyanide, using uranium nitrate as outside indicator and a volume of 200 cc. at the end point with the following results:

10 cc. of zinc = 9.75 cc. of ferrocyanide
20 cc. of zinc = 19.13 cc. of ferrocyanide
30 cc. of zinc = 28.50 cc. of ferrocyanide
40 cc. of zinc = 37.87 cc. of ferrocyanide

From which

$$\begin{aligned} 28.50 - x &= 3(9.75 - x) \text{ and } x = 0.375 \\ 28.50 - x &= 3/2(19.13 - x) \text{ and } x = 0.40 \\ 19.13 - x &= 2(9.75 - x) \text{ and } x = 0.37 \\ 37.87 - x &= 4(9.75 - x) \text{ and } x = 0.38 \\ 37.87 - x &= 4/3(28.50 - x) \text{ and } x = 0.39 \\ 37.87 - x &= 2(19.13 - x) \text{ and } x = 0.39 \\ \text{Average, } &0.38 \text{ cc.} \end{aligned}$$

The ratio of the zinc solution to the ferrocyanide solution after subtracting the blank of 0.38 cc. figures out as 1 to 0.937.

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The Reactivity of Coke

An Improved Method for Determining the Reactivity of Coke in Carbon Dioxide

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IN THE investigation of the gas-, coke-, and by-product-making properties of American coals, thirty coals have been tested by the Bureau of Mines-American Gas Association method (4) at carbonizing temperatures of 500°, 600°, 700°, 800°, 900°, 1000°, and 1100° C. The charges are large enough so that the structure of the coke is similar to that produced industrially. Certain physical and chemical properties of the carbonization products have been reported (4); this investigation of the reactivity of the cokes is a continuation of such studies.

Development of the Method

A wide variety of methods for determining the reactivity of coke is available, most of them using carbon dioxide or air as reactants and a few using steam. The Bureau of Mines used all three media in a previous study (3) but prefers carbon dioxide because it does not have the disadvantage of large dilution with an inert gas. Steam is particularly applicable where it is desired to test the coke as water-gas fuel. Carbon dioxide was adopted for the present study.

The temperature at which reactivity usually is measured is 900° to 950° C., which is approximately that at which high-temperature cokes are made. Heating to a higher temperature than that used in manufacture may change the structure and chemical composition of the coke, which will influence the determination of initial reactivity. In comparing the reactivities of cokes made at temperatures from 500° to 1100° C. it was necessary to obtain initial reactivity as nearly as possible, since low-temperature cokes change structurally and chemically on reheating, as will be shown. Also, the reaction temperature chosen must be high enough to distinguish between the insensitive high-temperature cokes and yet not approach the upper theoretical limit for low-temperature cokes. Time of heating is also a factor.

CHANGES IN LOW-TEMPERATURE COKES CAUSED BY REHEATING TO HIGH TEMPERATURES. The first method considered involved bringing a 10.5-ml. sample sized to pass 10-mesh and remain on 20-mesh to 950° C. in nitrogen, which required about 1 hour, flushing out the nitrogen with carbon dioxide, and then passing exactly 100 ml. of carbon dioxide in 20 minutes. The gas from this final 100 ml. of carbon dioxide was collected in a buret over potassium hydroxide, which absorbed the excess. The residual gas, presumably pure carbon monoxide, was measured and its amount reported as per cent reactivity. Residual gases from several low-temperature cokes tested in this manner contained appreciable amounts of hydrogen and methane.

Devolatilization tests at 950° C. were then made on three cokes from Sewell bed coal, which were heated in nitrogen from room temperature to 950° C. in 70 minutes. The gases evolved were collected over dilute sulfuric acid and analyzed.

The results of these tests are given in Table I. The gases continued to be evolved in appreciable amounts from each of the cokes for 4 hours, and although the initial rate of evolution was much the lowest for the 900° coke, the rates were all of the same order after the second hour. From the gas analyses it is clear that sufficient carbon monoxide is evolved in a 10- to 20-minute test to affect any reactivity result seriously unless correction is made for the evolved gas. For example, if one should make a test at 950° C. on 10.5 ml. of coke carbonized at 900° C. devolatilized by heating in nitrogen at 950° C. for 1 hour, 0.79 ml. of gas would be evolved per minute; the total gas in a 20-minute test interval would be 15.8

ml. The volume of carbon monoxide would be 2.55 ml. Obviously it will be impractical to determine reactivity of coke accurately by any method involving the direct use of carbon monoxide content of the gases from the test as a measure thereof.

TABLE I. GASES EVOLVED FROM COKES ON REHEATING AT 950° C.

Time Heated at 950° C., Hours	(Coal No. 27) Average Rate of Gas Evolution during 1-Hour Periods, Cc./Min./10.5 Cc. of Coke		
	500° coke	700° coke	900° coke
1		Gas not collected	
2	1.52	1.45	0.79
3	0.57	0.55	0.48
4	0.45	0.31	0.40
Gas evolved	Analysis of gas ^a		
	%	%	%
CO ₂	0.2	0.5	0.4
H	75.3	75.6	76.9
CO	15.6	15.8	16.2
CH ₄	2.4	2.1	1.5
N	6.3	6.0	5.0
Total gas collected, cc.	152	139	100

^a Gas from 500° and 700° cokes during 3rd and 4th hours, from 900° coke during 2nd, 3rd, and 4th hours.

Additional data on the gases evolved on reheating were afforded by a carbonization test in which a 70-pound charge of coke made from Freeport coal at 600° was cooled in the retort and then recarbonized at 1000° C. The time required for recarbonization was 2 hours and 53 minutes, and the yields of volatile products were: 3.9 per cent gas, 0.7 per cent tar, 0.05 per cent light oil, no liquor, and 0.04 per cent ammonia. The yield of gas on the volume basis was 5100 cubic feet per ton of coal originally charged, and most of this gas was hydrogen (Table II).

TABLE II. GAS OBTAINED ON RECARBONIZING A CHARGE OF 600° COKE AT 1000° C.

Gas	%
CO ₂	0.7
Illuminants	0.6
O ₂	0.9
H ₂	83.3
CO	3.8
CH ₄	7.1
C ₂ H ₆	0.0
N ₂	3.6
Total	100.0

The shrinkage of the charge as a whole due to recarbonization was approximately 5 per cent, but the shrinkage of actual coke substance probably was minimized by development of radial fissures in the monolithic charge which would cause apparent expansion.

SHRINKAGE OF COKE SUBSTANCE ON REHEATING. Under the reactivity test conditions first selected—that is, heating to 950° C. in nitrogen in 1 hour—shrinkage was observed for several cokes from coals of different ranks, illustrated by the results for Illinois No. 6 coal given in Table III.

TABLE III. SHRINKAGE OF COKES FROM ILLINOIS COAL ON REHEATING TO 950° C. IN REACTIVITY TEST

Carbonizing Temperature ° C.	Shrinkage %
500	21
600	21
700	10
900	3
1100	nil

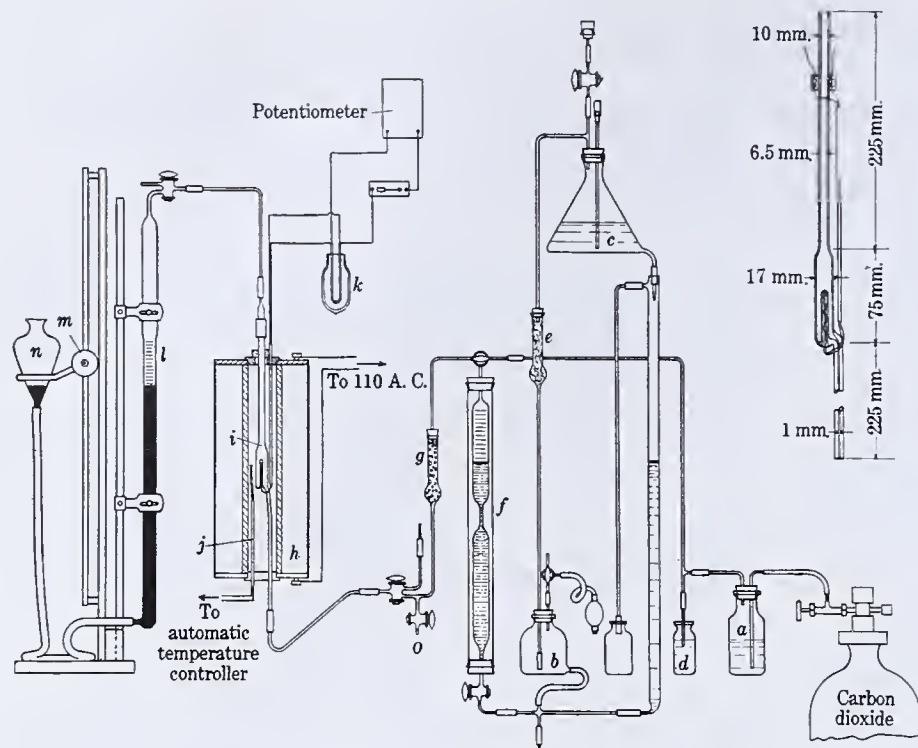


FIGURE 1. DIAGRAM OF APPARATUS

Since no fissures developed in the particles of coke and no new particles finer than 20 mesh were produced, the shrinkage obtained represented actual shrinkage of the coke particle. Furthermore, it appeared on comparison of the heated and unheated cokes under the microscope that the size of exposed cells had diminished. On reheating cokes from Summerlee coal shrinkage began at approximately 700°, was most rapid between 700° and 760°, and was practically uniform between 760° and 900° C.

Obviously, reheating low-temperature cokes tends to cause both chemical and structural changes which may affect the reactivity result obtained. Therefore, when data on initial reactivity are wanted it is desirable to have the test temperature as low as practical, to reduce the heating time as much as possible, and to reduce the "dead space" in the reaction tube to a minimum, so that the time for sweeping out the nitrogen may be decreased.

SIZE OF COKE AND RATE OF PASSAGE OF CARBON DIOXIDE. Previous experience had shown that reactivity could be determined satisfactorily with 10 to 15 ml. of 10- to 20-mesh (U. S. standard sieve) coke, passing 5 ml. of carbon dioxide per minute. This rate, which was continued throughout this investigation, is equivalent to a flow of 0.5 ml. of gas per ml. of coke per minute and is approximately the same as that used by Jones, King, and Sinnatt (5) in their standard method for determining reactivity of coke in carbon dioxide. With slight modification the writers have adopted the method used by these investigators for measuring and passing the carbon dioxide into the reaction tube.

DESIGN OF REACTION TUBE. A fused silica tube was designed so that the dead space to be swept out in starting a test would be small as possible, and was made with a bulb of size just sufficient to contain the sample of coke. A capillary tube was sealed to one end of the bulb for introducing the gas, and a tube of larger bore was sealed to the other end for charging the sample. A thermocouple well was fused into the bulb or coke chamber, extending half-way to its center. This permitted charging the coke, already contained in an inert atmosphere, into the preheated furnace, with the thermocouple in place, thus exposing the coke to the test temperature for a minimum time before the test was begun. Those methods in which the coke is charged into a cold fur-

nace and the whole system heated gradually to the test temperature may be criticized if used for testing low-temperature cokes, because of changes brought about in the coke by prolonged heating.

CHOICE OF REACTION TEMPERATURE. As a basis for choice of the reaction temperature tests of cokes from several coals were made at 800°, 850°, 900°, and 950° C. At 800° most high-temperature cokes are so slightly reactive that no differences are apparent. At 900° and 950° C. the low-temperature cokes are generally so highly reactive that all approach the upper limit of reactivity for a practical rate of gas flow. The results at 850° C. for both high- and low-temperature cokes are well distributed over the theoretically possible range, and therefore this was the test temperature adopted. Reactivities are expressed as the per cent of carbon dioxide converted to carbon monoxide.

Apparatus and Procedure

The apparatus finally adopted is shown in Figure 1. The water-jacketed buret, *f*, is constricted at the middle so that the volume of each half is 100 ml., and is connected to a vertical tube of uniform bore into which a saturated solution of magnesium chloride may flow from the reservoir, *c*. This reservoir is fitted with a capillary drain and an adjustable air inlet tube by which the flow of liquid into the buret may be regulated. The lower bottle, *b*, to which the aspirator bulb is connected, serves as a receiver for the solution in the buret as it is displaced by carbon dioxide. The solution may be forced from this bottle by air pressure upward through the glass wool filter, *e*, and into the reservoir, *c*. Capillary glass tubing connects the buret to the calcium chloride drier, *g*, and thence to the inlet of the silica reaction tube, *i*.

The reaction tube assembly is shown in detail in Figure 1. The inlet is capillary silica and the outlet of small-diameter silica with a bore large enough to permit charging and discharging the granular coke. The volume of the coke chamber is 10.5 ml., and the total volume of the silica assembly, including inlet and outlet tubes, is 18.5 ml. A small, thin-walled silica tube with closed end is sealed into the lower end of the coke chamber, projecting to its center, to serve as a thermocouple sheath.

The furnace is heated electrically and is provided with an automatic temperature controller. That portion of the furnace containing the coke chamber was tested under conditions of automatic control and found to be heated uniformly.

The silica tube outlet, which also serves for charging and dis-

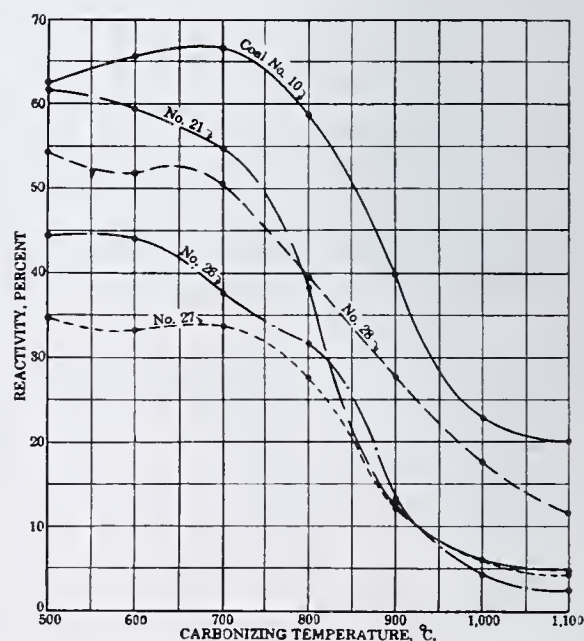


FIGURE 2. RELATION OF REACTIVITY OF COKE TO CARBONIZING TEMPERATURE

TABLE IV. ANALYSIS AND PLASTIC PROPERTIES OF COALS
(In order of decreasing fixed carbon in coal)

Coal No.	Bed	State	County	Dry Mineral-Matter-Free Fixed Carbon %	Moisture %	Proximate Analysis (as Carbonized Basis)			Modified Layng-Hathorne	
						Volatile matter %	Fixed carbon %	Ash %	Plastic range ° C.	Maximum pressure, mm. of water
26	Sewell	W. Va.	Raleigh	78.6	1.3	20.8	75.8	2.1	119	600
27	Sewell	W. Va.	Fayette	72.5	1.9	26.5	69.2	2.4	133	910
28	Pittsburgh	Pa.	Fayette	62.6	1.8	35.1	57.7	5.4	61	340
10	Illinois No. 6	Ill.	Franklin	60.6	7.9	32.1	47.7	12.3	45	26
21	Green River	Ky.	Muhlenberg	57.0	10.1	36.2	47.0	6.7	49	55

charging, is connected as shown to a glass capillary leading to a mercury-filled buret of 200-ml. capacity, which serves to collect the gaseous products of the reaction. A leveling bottle mounted on a suspension arranged to travel over a gear rack permits adjusting the level of the mercury in the buret uniformly and slowly.

A 10.5-ml. sample of coke was used for each test. It was poured through the silica charging tube into the reaction chamber and settled with slight tapping to the junction of the chamber and the tube. As the furnace was vertical the charged coke particles were not free to move, and the fuel bed was uniform at the beginning of all tests. The coke did not enter the capillary gas-inlet tube. After charging, nitrogen was passed through the coke to displace the air.

With the furnace previously heated to 850° C., a cap was placed on the charging or outlet tube, and after the rubber tubing connecting the capillary to the nitrogen cylinder was removed the charge was placed in the furnace. The connection to the capillary inlet was made, the cap removed from the outlet, and connection made to the mercury-filled buret. The 3-way cock of the latter buret was left open to permit the escape of gases while the coke chamber was coming up to temperature.

The magnesium chloride solution was forced up into the reservoir, c, and the air inlet of this reservoir was set at a point (pre-determined) which insured the required drip of solution to expel the carbon dioxide from the buret at the test rate of 5 ml. per minute. The volume of the carbon dioxide in the lower half of the buret was reduced to exactly 60 ml., and the test was started exactly 5 minutes after charging, this period being sufficient to bring the temperature of the coke up to 850° C. With the liquid in the tube at the same level as that in the buret, thus insuring atmospheric pressure therein, the gas flow through the coke was started, the effluent gases being vented at the 3-way cock. During the 12-minute period in which the gas from the lower half of the supply buret was displaced, the temperature and the rate of gas flow were checked. As the last of the gas was expelled the 3-way cock was turned so that the effluent gases collected in the buret, and during the remainder of the test atmospheric pressure was maintained inside the system by slowly lowering the mercury reservoir.

With the carbon dioxide flowing at the rate of 5 ml. per minute the time required for a determination was 20 minutes. After a little experience it was not difficult to obtain good adjustment of the rate, and the test periods, which were all timed, were close to that required. After passage of exactly 100 ml. of carbon dioxide the collected gases were measured and analyzed for carbon dioxide, that found being the residue not reacting with the coke. The difference between this volume and 100 is equal to the per cent of carbon dioxide reacting and is the reactivity sought. Each result reported is the average of two determinations agreeing to within 1.0 per cent. In a few cases it was necessary to make more than two tests because of wider variations.

Cokes Tested

The cokes selected for study were made from samples representing five ranks of coking coals according to the proposed classification of the American Society for Testing Materials (1). The proximate analyses of these coals and their plastic properties as determined by the Layng-Hathorne

method are shown in Table IV. The coals were carbonized by the Bureau of Mines-American Gas Association method. Chemical analyses and certain physical properties of the cokes have been published (4), but since no relationship was noted between these properties and the results of the reactivity tests they are not included here.

Results of Tests

Table V and Figure 2 show the results obtained by this method. Cokes made at 500° have reactivities of 34.6 to 62.8 per cent. The 600° cokes are of nearly the same order of reactivity as those made at 500°, four being slightly less reactive and one (No. 10) slightly more reactive. Of the 700° cokes, three decrease in reactivity from that obtained at 600°; No. 10 increases, whereas the reactivity of 700° coke from coal No. 27 remains approximately the same as the 500° and 600° cokes from this coal. The reactivities of all the cokes decrease as the temperature of carbonization is raised to 800°, 900°, and 1000°. The 1100° cokes generally are less reactive than those made at 1000°, but this difference is marked only in the case of the reactive No. 28 and No. 10 cokes. Summarizing these results, it may be concluded that reactivity of coke from a given coal decreases with increase in the carbonizing temperature and that this decrease is most marked between carbonizing temperatures 700° and 900°.

There is no direct relation between the fixed-carbon content of the coal (Table IV) and the reactivity of the corresponding coke. While it may be true that the rank of a coal affects the reactivity of the coke made from it, other factors are apparently of sufficient influence to change entirely the order in which reactivities of cokes align themselves in relation to this property in the coals.

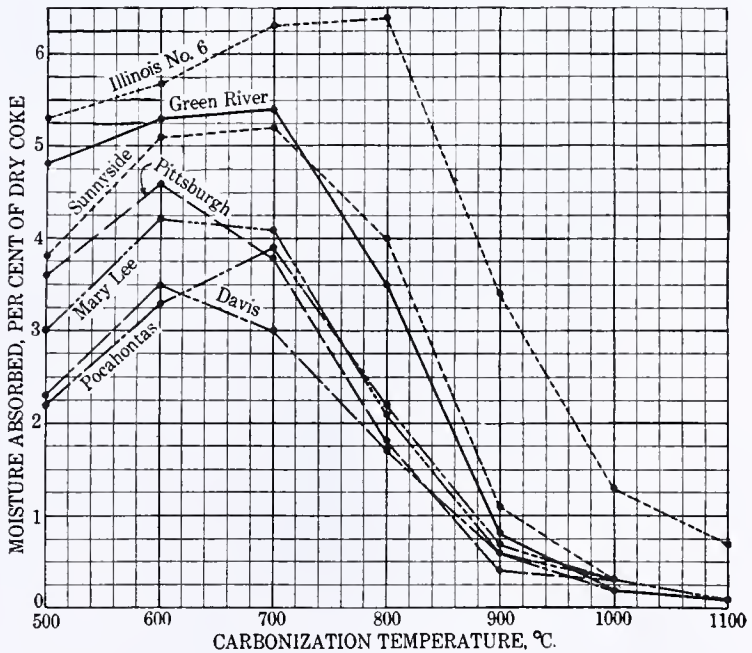


FIGURE 3. ABSORPTION OF MOISTURE BY COKES, 4- TO 10-MESH

TABLE V. REACTIVITY OF COKES IN CARBON DIOXIDE AT 850° C.

Coal No.	Carbonization Temperature, °C.						
	500	600	700	800	900	1000	1100
10	62.8	65.8	66.9	58.7	39.9	22.9	20.1
21	61.9	59.4	54.7	38.4	12.7	6.4	4.9
28	54.1	51.8	50.7	39.3	27.9	17.7	11.5
26	44.1	44.0	37.5	31.7	13.2	4.3	5.0
27	34.6	33.3	33.9	27.9	12.1	6.6	4.4

These cokes were among those used by Davis and Auvil (2) in their study of electrical conductivity. They found that the electrical conductivity of the 800° cokes increases and the plastic range decreases in the order No. 10, 21, 28, 26, and 27, which is also the order (Figure 2) of reactivity in which the 500°, 600°, and 700° cokes align themselves. It is not true that cokes made from coals of different rank invariably will have reactivities aligning with rank.

RELATION OF REACTIVITY TO HYGROSCOPICITY OF COKE. Reynolds recently published results (6) of an investigation of the hygroscopicity of cokes made at different carbonizing temperatures by the Bureau of Mines-American Gas Association method. Two of the series of cokes used (coal No. 10 from Illinois No. 6 bed and coal No. 21 from Green River

bed) were the same samples used for the reactivity tests given in this paper. The curves showing change of hygroscopicity with carbonizing temperature (Figure 3) and reactivity (Figure 2) exhibit similar trends. The main difference relates to the 500° cokes, which are invariably of lower hygroscopicity than those made at 600°, whereas this drop in reactivity occurs in only one case. The curves for Illinois coal are conspicuously high in both cases.

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Quantitative Analysis of Mine Dusts

An X-Ray Diffraction Method

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IN ORDER to study occupational diseases—silicosis, silicatosis, etc.—in relation to the constituents of mine or factory dusts, it is necessary to have exact quantitative knowledge concerning the chemical composition of the materials entering the lungs of workers. It has been pointed out repeatedly that the mineralogical composition, or state of chemical combination, of the factory or mine dust is of considerable importance in relation to the occurrence of these diseases, while the elementary composition—the chemical elements present—is of relatively little importance. An absolute, dependable method of quantitative mineralogical analysis is necessary, therefore, in order to study effectively the occurrence of these diseases, and to set up satisfactory standards for the protection of workers who must labor in dust laden atmospheres.

Various methods, both chemical and physical (4, 5), have been proposed and used for this purpose, but they are either not of general application, or are susceptible to influences which may vitiate the results in many cases. The failure of the widely used and generally dependable petrographic immersion method to distinguish between free quartz and some other silicate minerals in the dusts of some Canadian gold mines was directly responsible, through the suggestion of T. L. Walker, director of the Royal Ontario Museum of Mineralogy, for the development of the method to be described here.

Hull (3) pointed out a number of facts concerning the diffraction of x-rays by powdered crystalline materials. Of these the most important is that each crystalline chemical compound, when pulverized and placed in a monochromatic beam of x-rays, gives rise to a "diffraction pattern," which may be registered photographically and which is unique for that compound. The same compound always gives rise to the same diffraction pattern which is different from the pattern

obtainable from any other compound or from an allotropic modification of the same compound. For a mixture of crystalline materials, each substance present gives its own pattern, regardless of the presence of the other constituents, and the resultant pattern is the sum of the patterns of all the constituent compounds. By proper resolution of such a complex pattern into its constituent parts it is found that x-ray diffraction is a most powerful method of qualitative analysis, in that it shows not only the elements present but also their true state of chemical combination.

It was suggested at the time that the method should be capable of development as a quantitative analysis by the use of diffraction patterns of known mixtures for comparison with the pattern of the unknown. Since that time (1), relative line densities have been used for a rough estimation of the amounts of the various compounds present in a mixture, but up to now no one has seen fit to apply the highly developed technic of quantitative analysis by ultraviolet spectroscopy to x-ray powder diffraction.

The method as developed here, for which the preliminary work has been previously reported (2), is an adaptation of the "internal standard" method (6) of ultraviolet spectroscopy to the Hull method of x-ray diffraction by a crystalline powder. A pure crystalline powder, known not to be present in the mixture being examined, is added to the unknown in a definite ratio, and the x-ray diffraction pattern registered by a suitable apparatus. The ratio of the density of a line of the substance sought to that of a nearby line of the added standard is determined photometrically. The ratio thus obtained is proportional to the line intensity of the substance sought, which in turn is proportional to the amount of substance in the mixture. By reference to a curve which is prepared empirically using mixtures of known composition, the percentage of the constituent sought is obtainable at once.

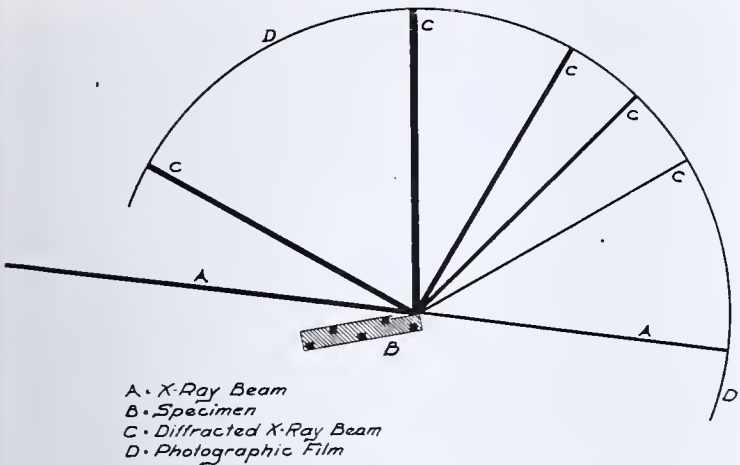


FIGURE 1. DIAGRAM OF X-RAY DIFFRACTION CAMERA

Apparatus and Diffraction Technic

For the registration of the diffraction pattern a circular reflection-type camera, shown diagrammatically in Figure 1, was used.

The specimen being examined was pressed into the shape of a wedge and mounted so that the tip of the wedge fell at the center of the camera. The tip of the wedge was bathed by the lower half of the main x-ray beam, which was defined by a series of lead pinholes 0.075 cm. (0.030 inch) in diameter. The resulting diffraction pattern was registered on a photographic film which was held tightly against the outside of a machined circle of which the tip of the wedge was the geometric center. It is observed that in certain directions from the wedge there is a focusing effect which causes a narrowing of the diffraction lines in these directions. By taking advantage of this, a high degree of resolution can be obtained in any desired portion of the pattern, together with a rather uniform background blackening in the region particularly to be investigated.

Figure 2 shows a camera of the type used in this work, arranged so that the wedge-shaped specimen may be revolved about its tip. This allows the side of the wedge next to the x-ray tube to be inclined at any angle to the incident beam of x-rays, so that the maximum effect of the focusing may be realized. Results may be duplicated exactly because the shape of the specimen is always the same, it can be set at the same angle to the beam every time, and all parts of the camera are permanently fixed with respect to each other and may be locked into position on the instrument table, so that conditions surrounding the registration of the diffraction pattern may be maintained at maximum constancy.

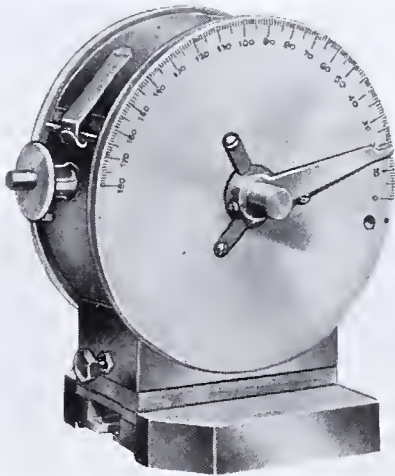
The specimen was irradiated with a Philips Metalix fine-structure-research x-ray tube with copper anode, mounted in a Hayes x-ray spectrograph, operating at 30 kvp. and 25 milliamperes. The exposure time varied from 1 to 6 hours, depending upon the concentration range of the specimen being examined, those specimens having the lowest percentages of the substance sought requiring the longer exposures.

Preparation of Samples

The natural ores and mine dusts submitted for analysis had been pulverized to pass a 200-mesh screen. Patterns for two of the dust samples as received, one high and one low in free quartz content, are shown in Figure 3, compared with patterns of pure rock crystal powder. The spotted lines showed that the average particle size was too large to give smooth diffraction lines. It was necessary to resort to some method of reducing the average particle size, for, unless smooth diffraction lines were obtained, photometer curves of the patterns would be meaningless. Furthermore, when it is considered that the amount of sample actually bathed by the x-ray beam is somewhat less than 1 mg., it is important to have an absolutely homogeneous speci-

men, with the added standard thoroughly incorporated with the sample. Both these ends were accomplished by developing a steel ball mill, using ball bearings in a cylindrical steel case, of such size that samples 1 gram in size could be handled without appreciable loss. Twenty-four hours' grind was found to be necessary to reduce quartz, which had already passed 200-mesh, to a powder of the required fineness.

The standard series of samples were prepared from powdered quartz and calcite, with the quartz content varying from 0 to 100 per cent. To cover the entire range, it was found necessary to divide it into three sections, the first extending from 0 to 10, the second from 10 to 60, and the third from 60 to 100 per cent. To 2 grams of the sample prepared as above, 0.5 gram of fluorite was added for the first two sections, and 1 gram for the third, as the internal reference standard, and the resulting mixture ground in the ball mill for 24 hours, using a high-boiling petroleum ether as a dispersion liquid to prevent caking of the powder. After grinding, the samples were freed of the petroleum ether, mounted in the diffraction camera, and the diffraction pattern was registered as described. A series of patterns for the 10 to 60 per cent range is shown in Figure 4.



Courtesy, J. B. Hayes, Inc.

FIGURE 2. X-RAY DIFFRACTION CAMERA

In the examination of the samples submitted for analysis, it was necessary to make preliminary patterns, to make certain that there were no lines present which would interfere with the desired line of the added standard and to determine by inspection the range in which the sample fell according to quartz content. The same relative amount of fluorite was added to the unknown as was used in the same range class for the standard series, and the resulting mixtures treated in the same manner as were the standard series.



FIGURE 3. PATTERNS FOR TWO DUST SAMPLES

Upper, mine dust No. 21 as received. Very low in quartz
Lower, mine dust No. 23 as received. High in quartz

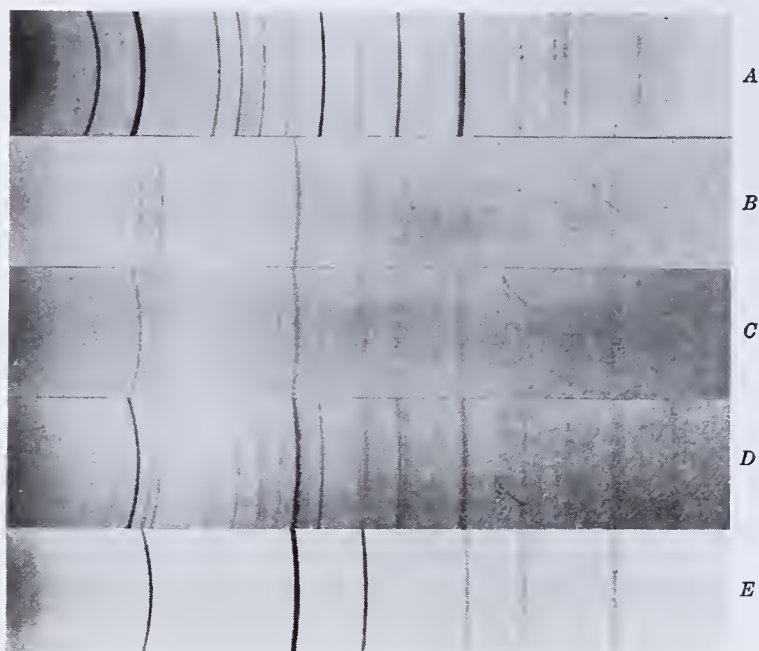


FIGURE 4. PATTERNS FOR 10 TO 60 PER CENT RANGE

A, pure quartz
B, 10 per cent quartz
C, 30 per cent quartz
D, 50 per cent quartz
E, fluorite

Measurement of Relative Intensities

The portion of each film containing the principal lines of quartz and fluorite was photometered using the Hayes microphotometer. The microphotometer is of the Moll type with a bismuth-silver vacuum thermocouple, and records photographically. From six to ten curves were made for each pattern at various points along the lines in order to get fair and dependable average measurements. A series of typical photometer curves is shown in Figure 5.

The density of a photographically recorded diffraction line may be considered as proportional to the height of its photometer curve above the general background of the pattern. If, for a series of samples, it is considered that all conditions surrounding the registration of the patterns are constant, the relative intensities of a given line appearing in all the patterns may be considered proportional to the relative densities of the line, and therefore proportional to the heights of the respective photometer curves. As it is practically impossible to control the conditions exactly, there will be some variation in density of a given line from film to film of the same sample. Small variations are satisfactorily taken care of by dividing the density of the line of the

substance sought by the density of a nearby line of the added standard. The ratios thus obtained are proportional to the relative intensities of the line, and hence to the concentration of the substance sought in the specimen. The theory underlying this discussion is fully developed by Scheibe in his excellent treatment of quantitative analysis with the quartz spectrograph (7).

The ratios obtained with the standard series for quartz are shown in Table I. Figure 6 shows the ratios plotted against the percentage quartz present in the standard samples. Duplicate runs on the standard series have not varied from the curve by more than 5 per cent of the amount of quartz present. For the lower percentages of quartz, there is a departure from the straight-line relationship observed in the other series. It has been determined that the smallest amount of quartz that can be identified positively using the technic described here is about 1 per cent, and it appears that the least amount that can be measured accurately is about 4 per cent. The method is certainly not to be recommended for traces. The reason for this is found in the multiplicity of lines of the other substances present in large amounts, which causes difficulty in the accurate placing of the base lines on the photometer curves.

In order to determine the influence of minerals other than calcite on the ratios, samples were prepared using picked crystals of zircon, titanite, and microcline in the place of calcite. These substances were chosen because, in addition to being silicate minerals, they give strong diffraction lines very close to those of quartz and fluorite, and contain elements of higher atomic number, with correspondingly higher absorption coefficients for x-rays, than calcite. The patterns of these minerals, together with those for their mixtures with quartz and fluorite, are shown in Figure 7. For zircon the

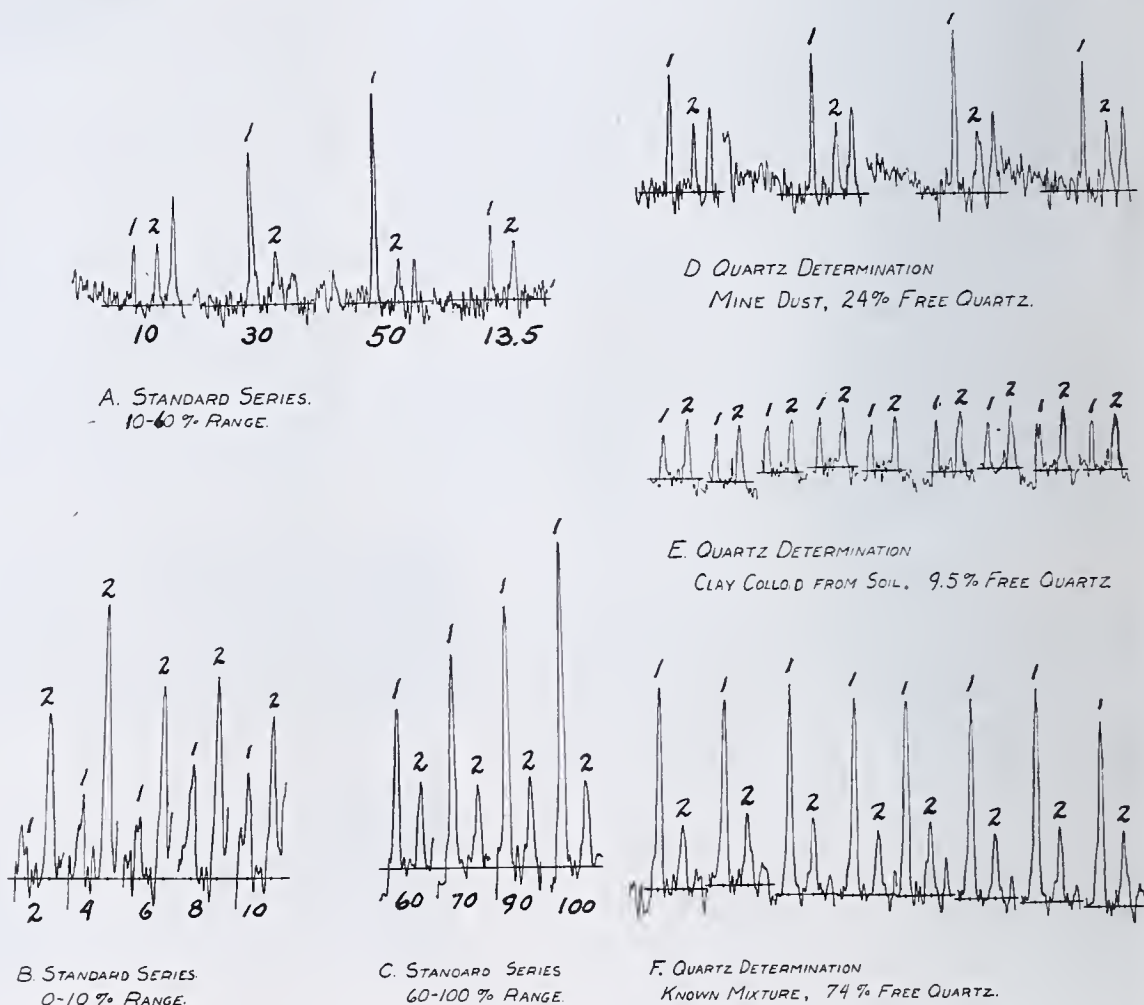


FIGURE 5. TYPICAL PHOTOMETER CURVES

1, quartz line 2, fluorite line

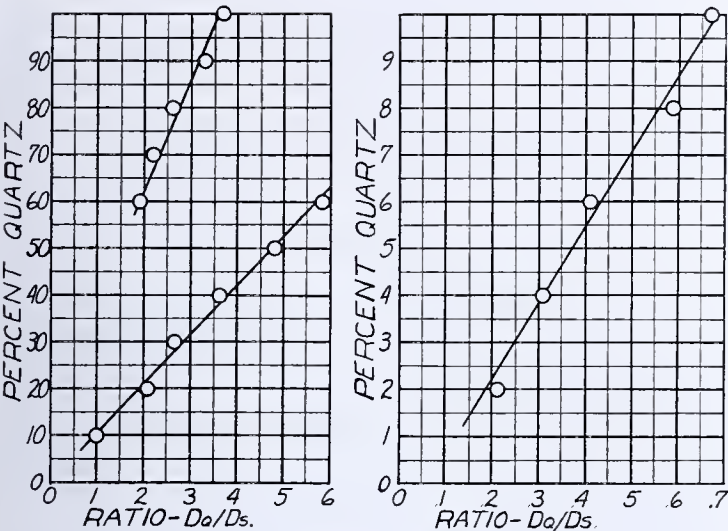


FIGURE 6. RATIOS
 D_q , density of quartz line D_s , density of standard line

strong quartz line and a strong zircon line almost coincide. The photometer curves for these patterns barely show resolution of the quartz line as an inflection point on the side of the curve for the zircon line. In the case of titanite and microcline, there are no coincident lines, but the lines are so numerous in the neighborhood of the quartz and fluorite lines used that some difficulty was experienced in fixing the base lines on the photometer curves.

TABLE I. STANDARD SERIES					
Sample	Composition			Quartz %	Ratio <i>D_q/D_s</i>
	Quartz	Calcite	Fluorite		
	<i>Grams</i>	<i>Grams</i>	<i>Gram</i>		
A. 0 to 10 per cent					
KC 1	0.04	1.96	0.50	2	0.21
KC 2	0.08	1.92	0.50	4	0.31
KC 3	0.12	1.88	0.50	6	0.41
KC 4	0.16	1.84	0.50	8	0.59
KC 5	0.20	1.80	0.50	10	0.67
B. 10 to 60 per cent					
KS 4	0.20	1.80	0.50	10	1.0
KS 5	0.40	1.60	0.50	20	2.1
KS 6	0.60	1.40	0.50	30	2.7
KS 7	0.80	1.20	0.50	40	3.6
KS 8	1.00	1.00	0.50	50	4.8
KS 9	1.20	0.80	0.50	60	5.8
C. 60 to 100 per cent					
KD 1	1.20	0.80	1.00	60	1.9
KD 2	1.40	0.60	1.00	70	2.2
KD 3	1.60	0.40	1.00	80	2.6
KD 4	1.80	0.20	1.00	90	3.3
KD 5	2.00	0.00	1.00	100	3.7

TABLE II. INFLUENCE OF OTHER MINERALS PRESENT				
Diluent	20 Per Cent Quartz		40 Per Cent Quartz	
	Ratio	Apparent per cent	Ratio	Apparent per cent
Calcite	1.7	20.0	3.0	40.0
Zircon	1.6	19.0	3.1	41.0
Microcline	1.8	21.0	3.0	40.0
Titanite	1.6	19.0	2.9	39.0

The results of these tests are shown in Table II. The indicated percentage of quartz is in no case more than 5 per cent from the true value, and the agreement is better for the higher percentages. This is undoubtedly due to the fewer number of lines from the foreign substances present, with less interference in fixing the base lines on the photometer curves. In general, the variation of 5 per cent may be taken as a measure of the precision of the method, and, since the method is almost entirely empirical, 5 per cent may be taken as its accuracy. This corresponds to the best work done with the quartz spectrograph as used for quantitative analysis.

Results of Analysis and Discussion

Some of the results of analyses of submitted samples are shown in Table III. This method cannot be considered

to estimate "free silica," but only that part of the free silica which is present as "free quartz." If a sample contains silica in any other crystal form or as a glass, this silica will not be estimated as quartz by this method. This may explain in part the discrepancies between the results by the x-ray method and the petrographic immersion method upon samples K7, K8, and K9. An extended comparison between the two methods is now under way, and will be reported at a later date.

A rather conclusive test of the accuracy of the method was made by Walker. Without the authors' knowledge, he submitted two samples of mine dust, along with a series of unknowns, which had previously been analyzed by the x-ray method, and to which he had added a known amount of rock crystal powder. The results of this test are shown in Table IV, which is taken from Walker's report (8). The results fall well within the 5 per cent limit determined above.

Although the data presented here have to do only with the estimation of quartz, there is no theoretical reason why any other mineral in a mixture could not be determined quantitatively, since the method is limited only by the necessity of having pure minerals available for the preparation of the series of standard samples.

Care must be exercised in the choice of a reference standard. The line of the standard to be used for comparison must be

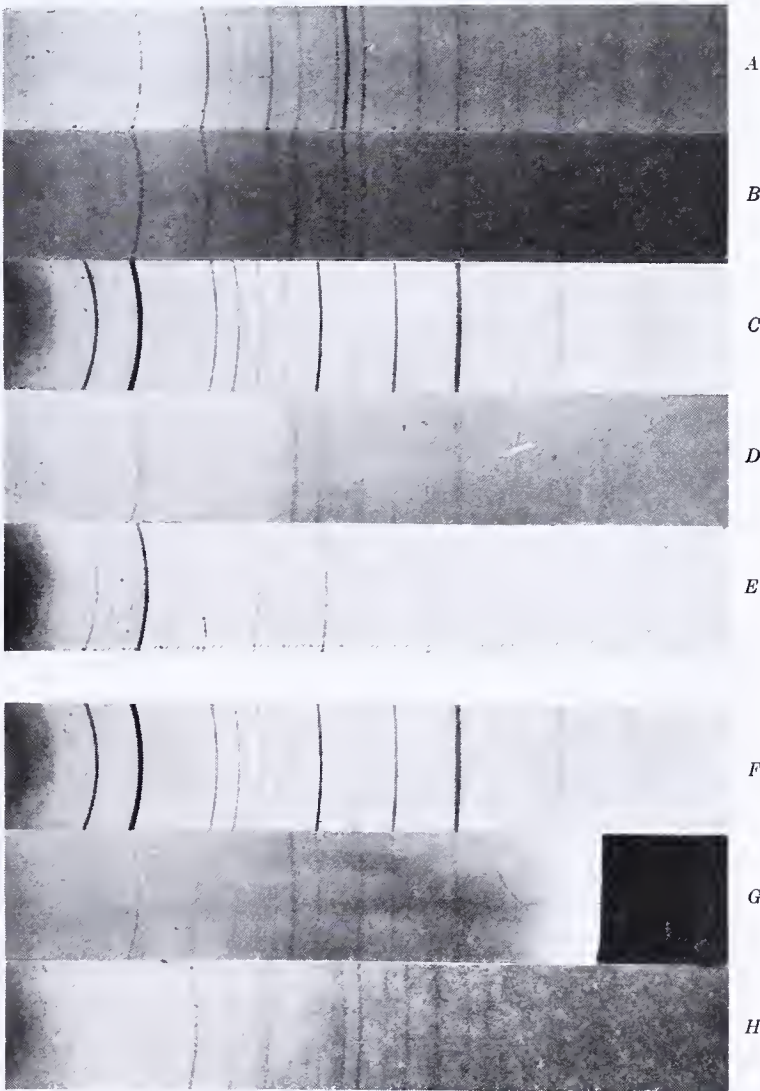


FIGURE 7. X-RAY PATTERNS
A, pure zircon
B, 60 per cent zircon, 40 per cent quartz, with fluorite
C, pure quartz
D, 60 per cent microcline, 40 per cent quartz, with fluorite
E, pure microcline
F, pure quartz
G, 60 per cent titanite, 40 per cent quartz, with fluorite
H, pure titanite

distinctly separated from lines produced by other minerals present in the sample to be analyzed, and it should be as near as possible to the line of the substance sought, so that the two will undergo the same absorption effects and will have nearly the same general background fogging. Using the technic described here, a separation of 0.3 mm. is satisfactory for good resolution. Since each crystalline substance present in the sample gives several diffraction lines, a suitable line may be found in almost every case for the satisfactory application of the method.

TABLE III. RESULTS OF ANALYSES

Sample	Material	Quartz	
		X-ray method	Microscopic method
		%	%
K 1	Mine dust	24.5	..
K 2	Mine ore	31.5	..
K 7 ^a	Feldspar	26.0	33.8
K 8 ^a	Corundum	Less than 1	0.8
K 9 ^a	Abrasive wheels	Less than 1	8.3
K 21	Mine dust	3.5	..
K 22	Mine dust	13.2	..
K 23	Mine dust	54.6	..
K 24	Mine dust	16.7	..
K 25	Mine dust	13.4	..

^a These samples were obtained from the Research Laboratories of the Aetna Life Insurance Company, Hartford, Conn., and were examined there for quartz by the petrographic immersion method.

TABLE IV. TEST OF X-RAY METHOD (8)

Sample	Quartz Found	Quartz Calculated
No. 2 with added quartz	37.0	35.5
No. 22 with added quartz	54.6	56.6

The apparatus used is necessarily expensive, but no more so than that required for dependable analysis with the quartz spectrograph. Aside from the time required for the long grinding operation, an analysis may be completed in about 4 hours.

The method should find ready application to many other industrial problems, such as those encountered in the manufacture of cement, plaster, and allied products, in identification and quantitative estimation of intermediate and final products in industrial processes, and in any case in which an

exact quantitative knowledge of the chemical or mineralogical composition of a mixture is necessary or desirable. The authors are at present using the method to study the kinetics of the change of some oxides from one allotropic form to another in the dry state, and it has been applied with success to the compounds of lead in storage battery research.

Summary

An empirical method for the quantitative analysis of mine dusts in terms of their mineralogical content using x-ray diffraction is described. A crystalline compound which is not present in the dust sample is added to it in a definite ratio. The densities of a diffraction line of the constituent sought and of a line of the added substance are compared photometrically. From the ratio the amount of the substance sought may be determined by reference to a curve in which similar ratios are plotted against per cent substance sought, the curve being prepared using synthetic standard samples of known composition. Duplicability of results is within 5 per cent of the amount of the substance sought in the case of quartz. The method has been applied only to quartz-silicate ore mixtures, ranging between 0 and 100 per cent, but should prove applicable to many other minerals.

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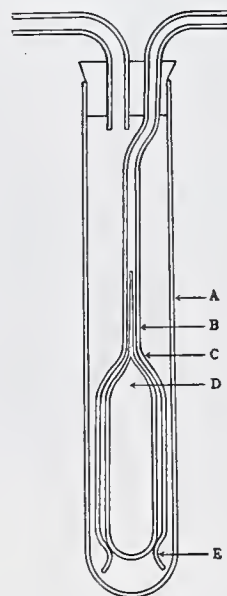
A Sensitive Check Valve

E. L. GREEN

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IN precipitating copper by hydrogen sulfide, a number of determinations were lost because of accidental interruption of the gas stream before all the solutions in the train had been saturated. Partial vacua developed where these unsaturated solutions took up the gas in the connections, and finally the solutions in the flasks backed up into the scrubbing devices. To prevent any such movement, an unusually sensitive check valve was required for the gas delivery tubes. The device illustrated has served this purpose.

The outer shell, A, is an ordinary 25-mm. (1-inch) test tube cut to a suitable length. B is made by sealing a piece of 4-mm. tubing to a piece of 15- to 18-mm. test tube of the indicated length. At point C the neck of part D is ground into B to an airtight seat. To avoid sticking, this joint should have a blunt rather than a



long taper. Part D is made from a 10-mm. test tube. A tail is drawn on the upper end to guide it into its seat. A tail on the lower end serves as a handle during the grinding and is then sealed off. When D is finished it must float less than half submerged in water. With D in place, the lower end of B is softened and three indentations are pressed into it to retain D.

In use, as small a quantity of water as will serve is placed in A. A current of gas entering through B displaces the water from it into A and D falls away from its seat. As soon as the current of gas tends to reverse, the water rises inside B and floats D into its seat. A reverse pressure too slight to close one of these valves but still capable of backing gas through it is impossible.

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Determination of Free Sulfur in Rubber

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SINCE the determination of free sulfur in vulcanized rubber is an analytical operation of utmost importance, any improvement in technic which increases the accuracy and also shortens the time required is of considerable value. In practically all the methods used in the past, the sulfur has been extracted with hot acetone and then determined by various means: direct weighing (2), oxidation and estimation as barium sulfate, conversion into thiocyanate and titration with silver nitrate (3), reaction of copper gauze with sulfur and iodometric determination of the hydrogen sulfide evolved when the gauze is treated with acid (4), treatment with alcoholic potash and estimation of the sulfide and thiosulfate formed (5). These methods usually require 8 hours or more for the extraction of the sulfur, and its estimation in the extract is a lengthy process.

Although much time is required for oxidation, precipitation, filtration, and weighing, the oxidation and gravimetric methods have proved best for routine work. Volumetric methods have not been satisfactory because of lack of satisfactory end points, side reactions, incomplete reactions, and tedious manipulations. The volumetric method to be discussed, however, makes it possible to shorten the time required for a free sulfur analysis to less than 3 hours per set of duplicate determinations.

In 1933 Bolotnikov and Gurova (1) introduced a volumetric method based on the fact that free sulfur is transformed into sodium thiosulfate when a rubber sample is heated in an aqueous solution of sodium sulfite. The authors have checked this method and have found the extraction and conversion into sodium thiosulfate to be complete and quantitative (as shown in Table I) in 2 hours when checked gravimetrically, using the Kratz, Flower, and Coolidge oxidation method on stocks containing non-sulfur-bearing accelerators.

TABLE I. CHECK DETERMINATIONS

Type of Stock	Free Sulfur	
	Gravimetric %	Volumetric %
Tube	0.36	0.36
Tube	0.94	0.95
Tire tread	0.22	0.22
Mechanical	1.21	1.24
Uncured rubber-sulfur mix	32.20	32.40
	32.40	32.50
	32.40	32.60

When the method of extraction of the sulfur and its conversion into sodium thiosulfate were found to be quantitative, the authors set out to simplify the procedure and to make it a rapid and practical one for routine testing of rubber stocks containing sulfur-bearing as well as non-sulfur-bearing accelerators.

Improved Volumetric Method

The presence of mercaptobenzothiazole causes the thiosulfate method to give high results (due to oxidation of mercaptobenzothiazole to benzothiazyl disulfide) when compared with corrected results from the Kratz, Flower, and Coolidge method, obtained by subtracting the sulfur content of the mercaptobenzothiazole present from the results obtained by their gravimetric procedure. The mercaptobenzothiazole content was determined for this correction by extracting the rubber sample with acetone, treating the extract with a benzene solution of cupric oleate, and estimating the precipitated cuprous salt of mercaptobenzothiazole gravimetrically (6).

Since the correction cannot be conveniently made in the volumetric method, it was decided to separate mercaptobenzothiazole from the sodium sulfite solution by precipitation. Although the various metals noted below form precipitates which may be filtered out, only the cadmium salt was found to be satisfactory in this case. Silver reacts with the thiosulfate to form silver sulfide. Lead thiosulfate is only sparingly soluble. Cuprous copper will react quantitatively with mercaptobenzothiazole, but any cupric copper will oxidize thiosulfate. Cadmium alone of all the metals tried precipitated mercaptobenzothiazole without reaction with thiosulfate.

The addition of 5 mg. of sodium stearate (which serves as a wetting agent in the extraction) and 0.5 gram of paraffin (which prevents frothing) were found to be beneficial. Air condensers are unnecessary, since cover glasses work satisfactorily when paraffin is used.

The fatty acids present in rubber stocks are extracted during the heating with sodium sulfite. These are precipitated along with the fatty acid from the soap by a solution of strontium chloride. The excess strontium forms insoluble strontium sulfite which helps to break up the other flocculent precipitates, thus keeping the filters from clogging.

Since the final titration is a thiosulfate-iodine reaction, it is necessary to eliminate or render inert the excess sodium sulfite. The addition of formaldehyde accomplishes this by forming a formaldehyde-sodium sulfite addition product.

The end point is improved by using a large volume (approximately 600 cc.) of solution acidified with acetic acid, and cooled below 15° C. with crushed ice. A very distinct end point is obtained which will last 2 to 3 minutes.

Procedure

Place 2 grams of thinly sheeted sample 0.05 to 0.075 cm. (0.02 to 0.03 inch) in a 400-cc. Underwriters' flask. Add 100 cc. of 5 per cent sodium sulfite solution, 5 cc. of a 0.1 per cent sodium stearate suspension in water, and approximately 1 gram of paraffin. Cover the flask with a small watch glass and heat so as to boil gently for 2 hours. Remove the flask and add 100 cc. of 0.5 per cent strontium chloride solution and 10 cc. of 3 per cent cadmium acetate solution. Separate the rubber and precipitates by filtration, using a Büchner funnel with suction. Wash with two 75- to 100-cc. portions of a wash solution containing 40 cc. of 3 per cent cadmium acetate solution per liter. (The funnels are prepared by forming a thin asbestos pad over a single sheet of qualitative filter paper. Filters thus prepared can be used numerous times.) To the filtrate, add with stirring 5 cc. of 40 per cent formalin solution, 10 cc. of glacial acetic acid, and 5 cc. of 1 per cent starch solution. Add enough crushed ice to bring the temperature of the solution below 15° C., and titrate with a standard solution of iodine to a blue end point. A blank determination is run on the reagents and this figure, usually 0.2 to 0.3 cc., is subtracted from the titrations on the samples.

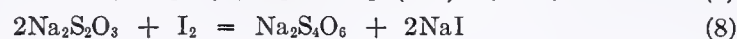
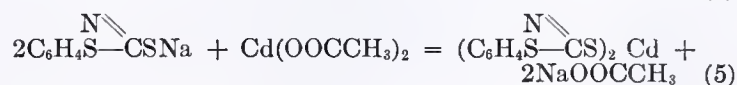
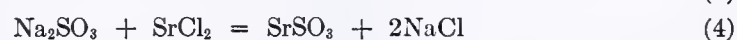
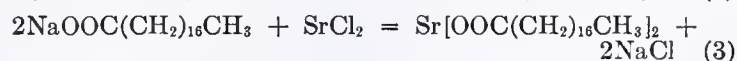
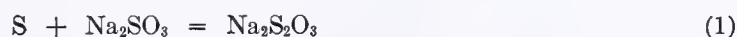


TABLE II. COMPARATIVE DETERMINATIONS

(Stocks containing non-sulfur-bearing accelerators)

Sample	Free Sulfur	
	Gravimetric %	Thiosulfate %
Tread	0.53	0.49
	0.49	0.44
	0.21	0.19
	0.36	0.35
	0.22	0.23
	0.07	0.07
	1.05	1.02
Cushion	1.00	0.99
	0.79	0.75
	0.75	0.71
Carcass	0.53	0.50
	0.25	0.22
	0.37	0.36
	0.20	0.18
Tube	1.00	0.98
	0.52	0.52
	1.02	0.98
	0.52	0.52
Valve bases	0.15	0.13
	0.52	0.51
	0.87	0.84
	0.88	0.87
	0.18	0.16
	0.04	0.05

TABLE III. COMPARATIVE DETERMINATIONS

(Stocks containing mercaptobenzothiazole)

Sample	Free Sulfur	
	Corrected gravimetric %	Thiosulfate %
Tread	0.15	0.16
	0.46	0.47
	0.11	0.15
	0.23	0.21
	0.54	0.52
	0.43	0.43
Carcass	0.20	0.22
	0.42	0.39
	0.82	0.78
	0.25	0.29
	0.26	0.24
	0.36	0.36
Tube	0.23	0.19
	0.11	0.07
	0.05	0.04
	0.01	0.01
	0.07	0.08
	0.75	0.78
Juvenile tires	0.43	0.46

From Equations 1 and 8 it is evident that one equivalent of iodine is required for each equivalent of sulfur; hence 1 cc. of a 0.1 *N* solution would be equal to 0.003206 gram of sulfur. It has been found convenient to use 0.0624 *N* iodine solution, so that 1 cc. is equivalent to 0.00200 gram of sulfur or 0.10 per cent free sulfur on a 2-gram sample.

Discussion of Results

A comparison of results obtained by both the Kratz, Flower, and Coolidge and the thiosulfate methods (Table II), on stocks containing non-sulfur-bearing accelerators, shows that the volumetric method usually gives results very slightly lower than the gravimetric, the maximum being 0.05 per cent on the compound.

A similar comparison (Table III) was made on stocks containing mercaptobenzothiazole as a representative sulfur-bearing accelerator of wide usage. The amount of sulfur in the acetone extract which was determined to be organically combined as mercaptobenzothiazole was subtracted from the gravimetric value to give the corrected gravimetric free sulfur value.

The comparative figures show an agreement between the two methods which is extremely good and within the experimental errors involved, and are offered as proof that the thiosulfate method obtains free sulfur values that are of practical worth in a minimum of time.

In addition to all common fillers, softeners, etc., the following compounds have no effect upon the accuracy of the method:

TABLE IV. DETERMINATIONS ON MERCAPTOBENZOTHAZOLE TREAD STOCKS

Gravimetric Free Sulfur %	Correction %	Free Sulfur	
		Gravimetric Free Sulfur Corrected %	Thiosulfate %
0.67	0.09	0.58	0.61
0.38	0.14	0.24	0.24
0.36	0.02	0.34	0.35
0.72	0.27	0.45	0.43
0.78	0.27	0.51	0.51
0.85	0.28	0.57	0.57
0.54	0.16	0.38	0.40

TABLE V. COMPARISON OF METHODS

Stock	Free Sulfur			
	Katz, Flower and Coolidge Corrected		Bromine	Thio-sulfate
	%	%	%	%
Guanidine	0.35	0.34	0.34
	0.72	0.70	0.69
	0.71	0.72	0.71
	0.79	0.74	0.74
Mercaptobenzothiazole	0.85	0.57	0.68	0.57
	0.72	0.45	0.56	0.43
	0.50	0.37	0.36	0.34
	0.26	0.10	0.18	0.13
	0.48	0.32	0.39	0.35

thiocarbanilide, guanidines, aldehyde amines, tetramethylthiuram monosulfide, mercaptobenzothiazole, benzothiazyl disulfide, *p*-aminophenol, naphthylamines, xanthates, carbamates, and vulcone.

Accelerators such as tetramethylthiuram disulfide, which also function as vulcanizing agents, liberate the available sulfur during the heating with sodium sulfite and the thiosulfate thus formed influences the accuracy of the free sulfur determination on such stock. This is perhaps no serious handicap because gravimetric results on such stocks are of no particular value because of the high percentage of organically combined sulfur in the acetone extract.

Conclusions

Values obtained by the volumetric method herein described compare favorably with those obtained by gravimetric methods when corrections are applied to the latter for the sulfur in the organic compounds in the acetone extract.

The precision of the method is excellent, as duplicates in each set usually check within 0.01 per cent of free sulfur on the compound.

This method is much faster than previous methods.

The cost of the reagents is low when compared with most other methods.

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RUSTPROOFING PAINTS. A number of experiments concluded in Germany tend to prove that the old method of red lead priming followed by two coats of good varnish constitute the most reliable rust protection for exposed iron and steel objects. German railroad specialists state that experience of many years has brought out nothing to improve on red lead as a rust preventive. Sand blast cleaning has been found to produce the best results.

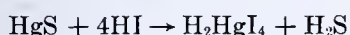
Accurate Separation of Precipitated Mercuric Sulfide and Sulfur in the Gravimetric Determination of Mercury

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THE common method for the determination of mercury as the sulfide suffers from the disadvantage that the precipitate is often contaminated with sulfur. The usual practice is to attempt to remove the free sulfur from the precipitate by various methods before weighing. Hot extraction with carbon disulfide is considered one of the best methods (3). Another is the successive washing of the precipitate with hydrogen sulfide water, hot water, alcohol, carbon disulfide, alcohol, and ether (1). All such procedures involve an element of uncertainty because of the difficulty of knowing when the removal of sulfur is complete, particularly since some forms of sulfur are but slightly soluble in certain of these solvents. The method of final treatment presented here avoids this possible source of error. It consists, in brief, of drying and weighing the precipitate without attempting to remove the free sulfur, treating it with cold concentrated hydriodic acid to dissolve out the mercuric sulfide without affecting the sulfur, and weighing this residual sulfur. The difference between these two weights gives the weight of pure mercuric sulfide present.

That hydriodic acid dissolves mercuric sulfide even in the cold was first observed by Kekule (2). With acid as concentrated as the constant-boiling mixture, hydrogen sulfide is vigorously evolved, and only a comparatively small volume is required to dissolve a given amount of the sulfide, the mercury going into solution in the form of a very soluble complex. The reaction can be expressed by the equation



Though this reaction proceeds even more vigorously with hot concentrated acid, the latter cannot be applied in this method because free sulfur reacts to a slight extent with it forming hydrogen sulfide and iodine. The cold acid apparently does not react with sulfur, at least during the short period of contact required in the practical procedure.

For this purpose hydriodic acid stabilized with hypophosphorous acid is the most convenient to use, since the rapid formation of troublesome free iodine from air oxidation is thus avoided. The hypophosphorous acid content in no way interferes with the separation. Merck's ordinary grade of specific gravity 1.70 was used in all the experiments recorded in this paper. The mercuric sulfide was prepared by precipitation of a solution of recrystallized mercuric chloride with hydrogen sulfide under conditions that led to the formation of no free sulfur. Samples treated with hydriodic acid gave no weighable residues. The specimen of pure finely divided sulfur was found to have no appreciable solubility in cold concentrated hydriodic acid. In testing this point the weighed samples of sulfur were placed in weighed glass crucibles, treated with about 5 ml. of the acid for several minutes with stirring, then washed with water and dried for 2 hours in a vacuum desiccator. In a typical run a 0.4225-gram sample left a 0.4222-gram residue after treatment, a difference of 0.0003 gram, which was probably in large part a weighing error.

Collect the precipitated mercuric sulfide in a weighed glass or porcelain filtering crucible, wash with cold water, dry thoroughly

at 110° C., and weigh. Replace the crucible in the holder without turning on the suction pump, and add cold stabilized constant-boiling hydriodic acid in the proportion of about 5 ml. for each gram of precipitate. Stir the mixture with a glass rod until all black particles of mercuric sulfide have disappeared, then turn on a gentle suction and draw the solution from the crucible. Wash the residual sulfur first with three or four successive 5-ml. portions of dilute (5 to 10 per cent) hydriodic acid and then with cold water. Water must not be used for the initial washings because of the danger of decomposing the soluble mercury complex, thus precipitating mercuric iodide in the pores of the filtering disk. Dry the crucible and its contents for about 2 hours in a vacuum desiccator and reweigh. The difference in the two weighings gives the amount of pure mercuric sulfide present.

Results from experiments on the quantitative separation of synthetic mixtures of mercuric sulfide and sulfur by this method are shown in Table I. The sharpness of the separation is evident.

TABLE I. SEPARATIONS OF MERCURIC SULFIDE FROM SULFUR

Mercuric Sulfide Taken Gram	Sulfur Taken Gram	Sulfur Found Gram	Error Gram
0.0865	0.4220	0.4221	+0.0001
0.1717	0.0822	0.0821	-0.0001
0.2099	0.0802	0.0801	-0.0001
0.3895	0.0052	0.0055	+0.0003

Apparently this method can be applied also to the rapid estimation of the mercuric sulfide content of technical grades of this sulfide prepared in the dry way, since, when genuine, these are mixtures of mercuric sulfide with more or less free sulfur. Results of test analyses of actual specimens are shown in Table II.

TABLE II. ANALYSES OF COMMERCIAL MERCURIC SULFIDES

Variety	Sample Taken Grams	Residue Found Gram	Mercuric Sulfide %
Black	0.5860	0.0275	95.31
	1.1210	0.0531	95.26
	0.3855	0.0182	95.28
	0.6103	0.0289	95.26
	0.4807	0.0226	95.30
Red	0.3748	0.0087	97.68
	0.7638	0.0178	97.67
	0.5385	0.0124	97.70
	0.4529	0.0104	97.70
	0.4768	0.0110	97.69

In these determinations the samples were weighed directly into weighed glass crucibles and treated by the above procedure. The very satisfactory agreement of duplicate trials on the same sample is evident. Since mercuric sulfide should be the only component in unadulterated commercial sulfides that is soluble in hydriodic acid, this method should also be highly accurate. Certainly it has the advantages of being much more rapid and much simpler than the usual procedures for the estimation of the mercuric sulfide content of such products.

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Determination of Formic Acid in Pyroligneous Liquors

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DETAILED study of the products and yields from the destructive distillation of agricultural wastes has necessitated repeated determination of the formic acid content of the pyroligneous liquors produced under different operating conditions. Methods of formic acid determination now in use are undependable or very time-consuming, when applied to such liquors, which usually contain comparatively small quantities of formic acid together with large quantities of other chemical compounds. These may interfere with or give positive reactions with the usual formic acid tests, and recommended prepurification procedures (3) have certain difficulties of application. There exists, therefore, a need for a convenient and accurate method for the determination of small quantities of formic acid in pyroligneous liquor.

Present methods of determining formic acid are, in general, based on steam-distilling the volatile components from the nonvolatile and then treating the solution with mercuric chloride and weighing the calomel precipitated (1); titrating the hydrochloric acid formed (5); estimating total acids before and after removal of the formic acid by oxidation with mercuric oxide (2); or estimating the carbon dioxide evolved by oxidation of the formic acid with mercuric oxide or other oxidants, using various methods of carbon dioxide absorption (2, 8). These methods are open to certain objections. Various impurities, especially aldehydes or unsaturated bodies that may act as reducing agents, will affect the calomel precipitation.¹ Gravimetric methods are likely to show relatively large percentage errors when the quantity of formic acid is small. Oxidation methods usually require the removal of dissolved carbon dioxide from the sample before subjection to the action of oxidizing agents, involving special apparatus

¹ The use of potassium acetate and hydroxylamine has been recommended as increasing the accuracy of the calomel method by J. C. Carlin of the Tennessee Products Corporation, Nashville, Tenn., but prepurification is required (private communication).

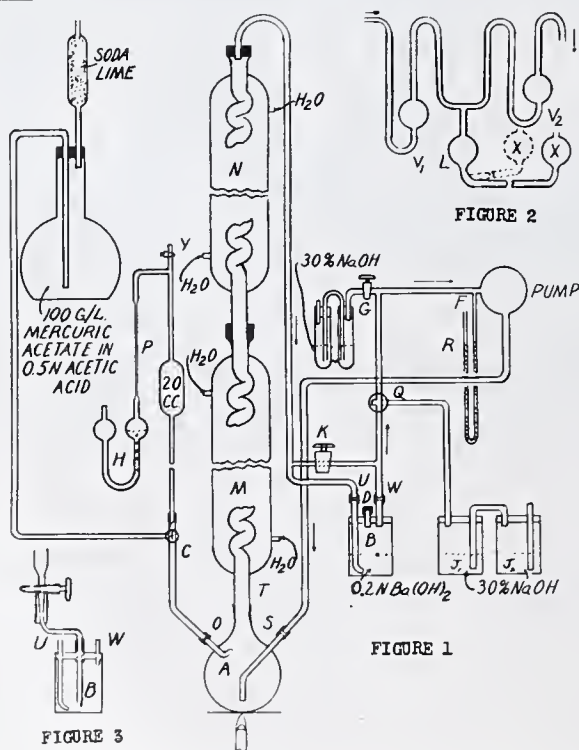
or procedure. The use of an insoluble oxidizing agent is attended by difficulties in preventing the admission of carbon dioxide from the air during addition, securing an even rate of oxidation, avoiding possible oxidation of impurities due to the excess oxidant present, avoiding loss of carbon dioxide due to failure of absorption systems of small capacity to take care of uneven liberation of gas, etc.

In the present experimentation, since an oxidation-carbon dioxide absorption scheme seemed to offer the greatest flexibility, various modifications of the methods now in use were studied in a effort to overcome known limitations. Various substances normally present in pyroligneous liquors were studied individually to ascertain the extent of error from such presence, and to learn how much preliminary purification is required for the accurate determination of formic acid under the conditions. After a trial the use of Truog towers (11) for absorbing carbon dioxide was abandoned because of difficulties resulting from absorption of carbon dioxide from the air during the washing of alkali from the tower, and in controlling the flow of carbon dioxide-free air at a uniform rate. A number of soluble and insoluble oxidizing agents were tried, and mercuric acetate solution, the addition of which can be easily controlled, was finally adopted as most suitable. Barium hydroxide solution was used for absorbing the carbon dioxide, which was estimated volumetrically. As a result of these experiments a closed circulatory absorbing system was evolved which is believed to minimize the disadvantages of other systems. It is cheap, easily constructed, easily regulated, and almost automatic in action, and, when it is once assembled, formic acid determinations may be performed rapidly, in sequence, about 30 minutes being required for an accurate determination on a pure or purified sample. Rates of oxidation, circulation, and absorption can be controlled at will without danger of admission of carbon dioxide from the air. Circulation may be maintained for any desired period, insuring complete absorption. Titration can be accomplished without air contamination, and various oxidants may be used as desired.

Various methods for removal of interfering impurities have been studied by other investigators, that of Fincke (3) appearing most adaptable for the present purpose. The method of formic acid determination here presented is a combination of the desirable features of several methods, especially those of Fincke (3) and Osburn (8), used in conjunction with an absorption apparatus evolved from one used by Partridge and Schroeder (9) for carbon dioxide absorption. It is believed that the proposed apparatus, with slight modification, may be applied to other organic determinations depending on measurement of evolved carbon dioxide.

Description of Absorption Apparatus

The proposed apparatus (Figure 1) consists of a 200-cc. Pyrex reaction flask, A, with one center and two side outlets. Above the center outlet, T, are mounted two spiral condensers, M and N, placed vertically, in series, and connected to the flask by a ground-glass joint. Through side outlet S is inserted an air-intake tube reaching nearly to the bottom of the flask, and joined to a pump system (Figure 2) as shown. The remaining outlet, O, is connected by means of a rubber tube to a three-way stopcock, C, permitting the addition of measurable amounts of the oxidizing solution through a 20-cc. pipet, which is connected



as shown for measuring and adding the oxidizing solution. To a side arm on the upper end of the pipet is attached a capillary tube, *P*, which retards to about 10 minutes the time necessary for emptying the pipet. To the other end of the capillary tube is attached a U-tube, *H*, containing sodium hydroxide solution. This tube serves the double purpose of removing all carbon dioxide from the air drawn through and of preventing the last few cubic centimeters of the solution from flowing into reaction flask *A*, thereby forming a liquid seal which prevents any carbon dioxide formed in the reaction from rising into the pipet. A cock at *Y* is opened to permit rapid filling of the pipet.

Evolved carbon dioxide passes through condensers *M* and *N* and is absorbed in titration bottle *B* (Figure 3). This is tightly closed by means of a three-hole rubber stopper, through which tube *U* brings the carbon dioxide air stream to the bottom, where it bubbles through the alkaline absorbing solution. Tube *D* allows addition of both the barium hydroxide and hydrochloric acid titrating solutions, while *W* is the exit through which the gas returns to the pump. A by-pass, *K*, is connected across *U* and *W* to allow pressure equalization.

*J*₁ and *J*₂ are two air-scrubbing bottles containing 30 per cent sodium hydroxide solution. During the preliminary period required for removing carbon dioxide from the system, carbon dioxide-free air in any required amount can be introduced through this scrubber and forced through the system by means of the pump, the air exit being at the upper end of tube *U*, where *B* is disconnected.

At *G* additional means is provided for releasing pressure or for admitting small amounts of air from which carbon dioxide has been removed by a scrubbing system containing sodium hydroxide. A mercury manometer U-tube, *R*, of rather small bore and registering pressure changes up to 100 mm., is attached at *F*.

Constant circulation of the enclosed air system is accomplished by a pump (Figure 2) consisting of an ordinary automobile windshield-wiper mechanism having a radial arm motion and bearing at the end of the arm a mercury reservoir, *X*, which is connected by glass and rubber tubing to a bulb, *L*. Vertical oscillation of reservoir *X* causes a fluctuating mercury level in *L*, forcing the enclosed gas in the system to circulate through two glass valves, *V*₁ and *V*₂, containing sufficient mercury for proper valve operation. This pump valve device is similar to one described by Maass (6).

Determination

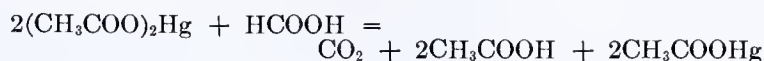
Steam-distill 25 cc. of crude pyroligneous acid and 5 cc. of sirupy phosphoric acid in a 500-cc. Claisen flask heated at 140° to 150° C. in a glycerol bath. (A somewhat more accurate procedure is to treat the original crude liquor with 20 per cent excess of *N* sodium hydroxide solution in a stoppered flask at room temperature for 24 hours, then acidify with phosphoric acid—5 cc. in excess—and distill as directed.) During the 2.5 hours (approximate) allowed for collecting the 1 liter of distillate, maintain the volume of liquor in the flask at about 10 cc. For formic acid determinations, neutralize 300 cc. of distillate (or a suitable aliquot containing from 0.05 to 0.1 gram of formic acid) to phenolphthalein with barium hydroxide solution and evaporate to dryness on the steam bath. (The remainder of this distillate is available for determination of methanol, acetic acid, acetone, and other constituents of the crude liquor.) Dissolve the residue in 50 cc. of warm water and transfer to reaction flask *A* (Figure 1). Add a small piece of paraffin (to reduce foaming) and 5 cc. of *N* acetic acid, and dilute the contents of the flask to about 100 cc.

Set stopcock *Q* so scrubbers *J*₁ and *J*₂ connect directly with intake valve *V*₁ of pump, and boil contents of flask for 10 minutes while passing carbon dioxide-free air through the solution and system to remove dissolved carbon dioxide. Connect titration bottle *B*, which contains a known quantity of standardized barium hydroxide (approximately 50 cc.), and continue boiling solution in the reaction flask. (Martin and Green, 7, add barium chloride to increase absorbing efficiency.)

Open three-way stopcock *C* and allow 20 cc. of the mercuric acetate oxidizing solution (Dissolve 100 grams of mercuric acetate in 1 liter of 0.5 *N* acetic acid and boil 1 hour to remove carbon dioxide. Keep tightly stoppered.) to flow slowly into flask, continuing circulation for 20 minutes. Stop pump and titrate contents of bottle *B* with standard 0.2 *N* hydrochloric acid (free from carbon dioxide) using phenolphthalein (Schollenberger, 10, recommends thymolphthalein.). Near the end point gently evacuate at *W* a few times, to draw solution from immersed tubing. Differences of pressure may be equalized at *K*, which should be open when pump is not operating and when bottle *B* is being connected or disconnected, to avoid drawing absorbing solution up into apparatus.

Calculation of Results

One cubic centimeter of 0.2 *N* barium hydroxide is equivalent to 0.0046 gram of formic acid.



Formic, acetic, or other volatile acids will carry over in the apparatus to a small extent causing absorption of alkali. The total correction for such volatilized acids under the conditions set forth was 0.04 cc. of 0.2 *N* alkali, which is so small that it may usually be disregarded. A blank determination will correct for this and for impurity of reagents.

Time Factor

During the development of the method it was found necessary to ascertain the time required to absorb all carbon dioxide evolved in the closed system during a determination.

After the apparatus had been freed from carbon dioxide, a solution containing 0.263 gram of dried anhydrous sodium carbonate dissolved in 25 cc. of carbon dioxide-free water was added to 75 cc. of carbon dioxide-free distilled water in flask *A* (Figure 1). Bottle *B* was then connected, and an excess of dilute sulfuric acid (free from carbon dioxide) was added to flask *A* through the pipet at *O*. At intervals of 5 minutes the pump was stopped, titration bottle *B* was changed, and its contents were titrated. Absorption occurred as follows:

	Cc. 0.2018 <i>N</i> Alkali Consumed
First 5 minutes	17.52
Second 5 minutes	7.04
Third 5 minutes	0.02
Total	24.58 (equivalent to 0.263 gram of sodium carbonate)

A 15-minute circulation is therefore ample for complete absorption of the carbon dioxide in the system, unless progress of the oxidation is retarded.

Effect of Certain Impurities

Crude pyroligneous acid consists of a mixture of water, tar, oil, formic, acetic, and higher acids, acetone, methanol, esters, ketones, aldehydes (especially formaldehyde, acetaldehyde, and furfural), acetals, phenols, pyridine, allyl alcohol, etc. Homologs and condensation and interaction products of these compounds are probably present, the percentages varying with the temperature of the destructive distillation. The acetic content is usually in excess of the formic. In the various existing formic acid methods which depend on oxidation many of these compounds may react, affecting the results in several ways: they may oxidize, yielding carbon dioxide; they may be carried over into the alkali and combine with it; or their presence may inhibit the liberation and oxidation of the formic acid.

Experiments were individually conducted with a number of these compounds to determine their behavior under the oxidation conditions of the method described herein. The results, shown in Table I, indicate that acetone, methanol, ethanol, glycerol, and lactic acid yield no carbon dioxide under the conditions of the method, while pyridine, allyl alcohol, acetaldehyde, "soluble" tar, "high-boiling" acid, unsaponifiable "chemical wood oil," oxalic acid, and various tar oil fractions and their phenols yield varying small amounts of carbon dioxide. Substances such as furfural and formaldehyde apparently oxidize slowly and yield carbon dioxide, the degree of oxidation depending on the time and concentration conditions. A previous saponification seems to be essential before the determination of the combined formic acid in formic esters, as in the case of the lower boiling compounds direct determination is often affected by unhydrolyzed ester passing out of the reaction flask.

TABLE I. OXIDATION BEHAVIOR OF INDIVIDUAL SUBSTANCES, UNDER LIMITS OF PROPOSED METHOD

Substance	Amount of Sample		Length of Run	Oxidizing Agent (Mercuric Acetate)	Carbon Dioxide Present		
	Grams	Cc.			Theoretical	Found	Per cent of theoretical found
			Min.	Grams	Grams	Grams	%
Acetone, C. P.	0.1	..	20	2	0.228	Trace	
	0.8	..	20	2	1.820	0.00045	0.02
Glycerol	1.25	..	20	2	None
Ethanol	50.0	20	2	None
Methanol, C. P.	0.08	..	20	2	0.11	Trace	
	0.80	..	20	2	1.1	0.00090	0.08
Oxalic acid, C. P. (anhydrous)	0.0833	..	20	2	0.0813	0.000976	1.20
	0.2	..	20	2	0.1956	0.00045	0.23
Lactic acid (analytical)	...	0.25	20	2	Trace
Pyridine (analytical)	4.95	..	10	2	13.77	0.00106	0.01
Furfural (technical redistilled)	1.16	..	20	2	2.66	0.01355	0.51
Acetaldehyde (redistilled)	0.80	..	20	2	1.60	0.000452	0.03 (affects alkali)
"Soluble" tar (from pecan shells)	0.1455	..	20	2	0.00227
"High-boiling acid" (Suida process)	0.5	15	2	0.0034	(essentially a mixture of propionic, butyric, and acetic acids and lactones)
"Wood chemical oil"	5.0	20	2	0.0216
Same (washed with sodium hydroxide)	10.0	20	2	0.0146
Corncob "chemical oil" (redistilled) fraction up to 136° C.	5.0	20	2	0.0213
Same, fraction 136° to 225° C.	5.0	20	2	0.00354
Peanut-shell tar oil (caustic-soluble portion, phenols)	5.0	20	2	0.00632
Formaldehyde (technical formalin)	0.1	..	30	5	0.1465	0.00236	1.95
			+ 30 ^a			0.00183	
			+ 30 ^a			0.00241	
			+ 30 ^a			0.00263	
			+ 30 ^a			0.00263	
Total			150			0.01236	8.44
Sample 2	0.06	..	30	2	0.088	0.00071	0.80
			+ 30 ^a			0.00217	
Total			60			0.00288	3.27
Sample 3	1.0	..	20	2	1.465	0.01845	1.26
Allyl alcohol (Eastman Kodak Co.)	4.27	..	90	2	9.71	0.013	0.13
			+ 20 ^a			0.00195	
Total			110			0.01495	0.15
Sample 2	4.27	..	10	2	9.71	0.001855	0.19
			+ 15 ^a			0.0063	
			+ 15 ^a			0.0042	
			+ 15 ^a			0.00177	
Total			55			0.014125	1.46
Sample 3	0.854	..	20	2	1.943	0.0108	0.56
Ethyl formate (basis 100% ester)	0.1306	..	30	2	0.0777 ^b	0.0772	99.4
	0.1306	..	30	2	0.0777 ^b	0.0777	100.0
	0.1306	..	30	2	0.0777 ^b	0.0780	100.4

^a Additional time periods on same experiment.^b Equivalent to carboxyl present. Saponified before determination.

The removal of soluble and insoluble tar from the crude liquor by a preliminary distillation before estimation of formic acid, etc., seems to be necessary (as shown in Table I), since the presence of tar also seems to affect the analytical procedure. Tests were therefore made to determine the quantity of distillate needed to effect total recovery of all the acids present in the crude, using the described procedure but analyzing successive 250-cc. portions of distillate. The average distribution of formic and total acid in the distillate was found to be as follows:

	Total Acid %	Formic Acid %
1st 250 cc. of distillate	92.87	95.87
2nd 250 cc. of distillate	4.44	3.29
3rd 250 cc. of distillate	1.87	0.84
4th 250 cc. of distillate	0.82	Not analyzed
	<u>100.00</u>	<u>100.00</u>

Because the results given in Table I indicated the necessity of removing certain interfering volatile constituents from this distillate before determining formic acid, experiments were undertaken to devise a convenient and efficient means for such removal (prepurification) without affecting the formic acid present. It was found that all the volatile interfering substances could be removed by neutralizing the acid mixture with barium hydroxide and evaporating to dryness on a steam bath. Since the barium salt of formic acid is stable at temperatures well above 100° C. (4), none is lost in this procedure, but more than a slight excess of barium hydroxide must be avoided. Results of tests with this prepurification treatment are given in Table II.

Discussion of Results

Table II shows the accuracy of the proposed method, as applied to pure formic acid solutions and to formic acid solutions containing interfering impurities, when determined with and without preliminary steam distillation and barium hydroxide pretreatment. For pure formic acid solutions, the direct determination gave an average experimental error of -0.24 per cent, the barium hydroxide treatment, when used, apparently not affecting these results. A combination of steam distillation and subsequent barium hydroxide treatment showed a +0.99 per cent error. The results secured on pure formic acid by substituting mercuric oxide for mercuric acetate were of similar accuracy. The results on sodium formate when determined alone showed a slightly greater error than when sodium acetate was added.

Experimentation with a test solution (solution A) containing known quantities of formic acid, acetic acid, formaldehyde, acetaldehyde, furfural, and allyl alcohol, the mixture representing a concentration of volatile interfering components normally present in the distillate from a crude pyrolygneous acid, gave results 3.17 per cent too high on direct determination of formic acid without steam distillation or pretreatment. When this mixture was subjected to the preliminary barium hydroxide treatment to remove volatile interfering substances, this excess value was reduced to +0.79 per cent. Experiments to show the extent of removal of interfering substances by steam distillation and by barium hydroxide treatment (combined or separate), when applied to a sample of crude pyrolygneous acid (solutions B and C).

indicated that with no pretreatment the results were 26 per cent higher than the actual formic acid percentage shown after the combined purification treatments. Barium hydroxide treatment alone, when applied to the same liquor, reduced the high value slightly, while subsequent steam distillation reduced this further to 13.1 per cent. Barium hydroxide pretreatment when applied subsequent to a steam distillation gave a value which is assumed to be the actual percentage of formic acid present.

Since the exact amount of formic acid actually present in a crude pyroligneous acid cannot be definitely established directly, the removal of formic acid from such crudes was studied by the expedient of adding formic acid to a crude liquor of low known formic content in known amounts and determining the recovery of this added acid, the amount not recovered being determined by difference. As shown in Table II, the percentage of formic acid not recovered by this procedure (per cent error) was less (2.3 per cent) when a saponification procedure was used than with the regular steam distillation only (3.4 per cent). Saponification of the crude liquor increased the amount of determined formic acid by about 20 per cent, indicating the presence of a significant quantity of formic esters.

Fincke (3) found that the recovery of formic acid by steam distillation, from mixtures other than pyroligneous acid, was not over 95 per cent even with prolonged distillation. Quantitative recovery of formic acid by the steam distillation of pure formic acid solutions is shown in Table II. It is probable that the recovery of formic acid from various complex mixtures will vary according to the physical and chemical properties of each mixture.

REMOVAL OF FORMALDEHYDE. Special attention was also given to the behavior of formaldehyde under the conditions of the proposed method. Since part of the formaldehyde vaporizes, and since the nonvaporized portion apparently oxidizes slowly to formic acid and subsequently to carbon dioxide under distillation, there are only two alternatives, either to oxidize it completely to carbon dioxide in the original liquid, or to destroy or remove it before making the determination, the recommended prepurification methods (distillation from tar and evaporation with barium hydroxide) apparently being satisfactory. A preliminary oxidation of the formaldehyde, by Fehling's solution, was tried. This reagent oxidized the formaldehyde to formic acid, but apparently did not oxidize the formic acid further to carbon dioxide. However, on subsequent oxidation with mercuric acetate, a portion of the excess Fehling's solution was oxidized to carbon dioxide, giving yields in excess of the theoretical. During the oxidation of the formaldehyde by the Fehling's solution no carbon dioxide was formed, although appreciable amounts of cuprous oxide were deposited. It may therefore be possible to determine the percentages of formaldehyde and formic acid in a mixture by selective oxidation.

Summary

A method is presented for the convenient determination of formic acid in pyroligneous acid, based upon the removal of certain volatile and nonvolatile interfering substances, followed by the oxidation of the formic acid to carbon dioxide in a closed system using mercuric acetate as oxidizing agent. The evolved carbon dioxide is absorbed by circulation of the enclosed air stream through standard barium hydroxide in a special apparatus, and the amount of formic acid (equivalent to the carbon dioxide absorbed) is calculated from titration data. This method determines small amounts of formic acid in pyroligneous liquors with an accuracy of about 97.0 per cent. Greater accuracy (over 99.5 per cent) is attained on pure formic acid solutions.

Mercuric acetate has been found to possess certain advan-

TABLE II. RESULTS OF PREPURIFICATION TREATMENT

Material Analyzed	Formic Acid Present Gram	Formic Acid Found ^a Gram	Error %	Barium Hydroxide Purification Treatment
Formic acid (pure)	0.0617	0.0616	- 0.16	No
	0.0617	0.0615	- 0.32	No
	0.0755	0.0756	+ 0.13	Yes
	0.0755	0.0751	- 0.53	Yes
	0.0814 ^(b)	0.0821	+ 0.99	Yes
	0.0814 ^(b)	0.0821	+ 0.99	Yes
Formic acid (c) (mercuric oxide substituted for mercuric acetate)	0.0656	0.0653	- 0.46	No
	0.0656	0.0656	0.0	No
Sodium formate, 0.1375 gram, equivalent to Sodium formate, 0.1375 gram plus 6 grams of sodium acetate, equivalent to:	0.0930	0.0940	+ 1.07	No
25 cc. of solution A ^(d)	0.0930	0.0930	0.0	No
	0.0378	0.0390	+ 3.17	No
	0.0378	0.0381	+ 0.79	Yes
	0.0378	0.0374	- 1.06	Yes
Solution B ^(e)		0.5280	26.0 (f)	No
		0.5200	24.1 (f)	Yes
Solution C ^(g)		0.4740	13.1 (f)	No
Solution C ^(g)		0.4190	0.0	Yes
Solution D ^(h)		0.0833		Yes
Solution D ^(h) (0.4968 gram of formic acid added)		0.0855		Yes
		0.570	- 3.4	Yes
		0.553	(average)	Yes
Solution D ^(h) (saponified)		0.0997		Yes
		0.1025		Yes
Solution D ^(h) (saponified and 0.4968 gram of formic acid added)		0.5822		Yes
		0.5858	- 2.3	Yes
			(average)	

(a) Calculated from carbon dioxide produced.

(b) Steam-distilled.

(c) Five grams of mercuric oxide used as oxidizing agent. The mercuric oxide was first added, carbon dioxide removed from the system, and the sample of formic acid, dissolved in carbon dioxide-free water, then added.

(d) Solution A consists of formic acid, 0.756 gram; acetic acid, 0.74; allyl alcohol, 0.18; furfural, 0.19; formaldehyde, 0.18; acetaldehyde, 0.18 in 500 cc.

(e) Solution B consists of a 100-cc. sample of original crude pyroligneous acid (undistilled).

(f) These values are calculated on the assumption that 0.4190 is the correct formic acid content.

(g) Solution C consists of distilled pyroligneous acid (total distillate from 100 cc. of same crude liquor as solution B).

(h) Solution D represents the formic acid found in the first 750 cc. of steam distillate from 25 cc. of crude pyroligneous acid (crude liquor from sample B). Saponification and addition of formic acid, where indicated, preceded steam distillation.

tages over mercuric oxide as an oxidizing agent, especially in the presence of dissolved carbon dioxide, because of its solubility in water.

The effect of interfering impurities on the method is shown. Impurities may for the most part be easily removed from distilled pyroligneous acid by neutralizing with barium hydroxide solution, followed by evaporation of the sample to dryness on a steam bath.

Preliminary saponification of crude pyroligneous liquors increased the formic acid percentages found, when formic esters were present.

A distillation procedure is described for removing volatile acids from crude pyroligneous acid.

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A Rapid Method for the Determination of Titanium

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BECAUSE of the increased use of titanium pigments, a rapid and accurate method for its quantitative estimation has become of considerable industrial importance. Gravimetric separations involving titanium are generally long and tedious because of the interference of many other common metals.

The general commercial method now in use involves the reduction of the titanium by means of a Jones reductor and subsequent titration with an oxidizing agent. However, because of the extreme susceptibility of the titanous ion to oxidation, the complete reduction and protection of the reduced titanium by this method requires over-large apparatus, a long period of time for the reduction, and a device for the protection of the reduced solution with carbon dioxide.

The method herein described gives quantitative results within 30 minutes and requires apparatus easily constructed from available laboratory glassware. Its use results in a saving of at least one-half of the normal time necessary for titanium determination by any of the standard methods now in use. It has been tested against samples of wide range of titanium content.

Discussion

Nakazono (1) developed an apparatus for the reduction of various ions using liquid zinc amalgam as a reducing agent. The use of a liquid amalgam has the advantage of exposing a greater area of zinc than could be obtained by a Jones reductor and therefore gave complete reduction in a much shorter time. The disadvantage of the Japanese method, however, was in the use of special apparatus which was not readily available. The authors have modified their apparatus so that it may be easily constructed from common laboratory glassware (illustrated).

The apparatus consisted of a 250-cc. globular separatory funnel, closed with a rubber stopper, *C*, carrying a piece of 0.63-cm. (0.25-inch) glass tubing, *B*, 5 cm. (2 inches) long which was stoppered by a small cork, *A*. The outlet tube of the funnel was connected to a 20- to 30-cc. glass tube, *D*, by means of a length of rubber tubing, *E*, which was closed by means of a pinchcock, *F*. Tube *D* was an old 25-cc. volumetric flask, but any small bulb may be used in its place.

After a number of experiments using both potassium permanganate and ferric ammonium sulfate as oxidizing agents for the titanous ion, it was found that ferric ammonium sulfate gave much superior results, probably because of the elimination of any iron interference. In general the method consisted of the reduction of the titanium to the trivalent state by use of liquid zinc amalgam and its titration with ferric ammonium sulfate using potassium thiocyanate as an indicator. The end point was the appearance of the usual wine-colored ferric thiocyanate complex.

Reagents

- 0.1 *N* potassium permanganate.
- Cooled, freshly boiled, distilled water containing 1 per cent of sulfuric acid.
- Ferric ammonium sulfate solution (approximately 0.7 *N*).
- Liquid zinc amalgam.
- Tablets of sodium bicarbonate (approximately 5-grain) purchased at any drug store.
- Potassium thiocyanate (saturated solution).

Procedure

The ferric ammonium sulfate reagent is prepared by dissolving 30 grams of the salt in 300 cc. of distilled water acidified with 10 cc. of sulfuric acid. Potassium permanganate solution is added drop by drop, as long as the pink color disappears, and the solution is then diluted to 1 liter. This solution is standardized, after reduction with zinc amalgam in the special reductor, by titration with standard potassium permanganate.

The zinc amalgam (1) is prepared as follows:

Fifteen grams of fine-mesh zinc well washed with dilute sulfuric acid are heated for 1 hour on a water bath with 300 grams of mercury plus 5 cc. of dilute sulfuric acid (1 to 4). After cooling, the amalgam is washed several times with dilute sulfuric acid. The liquid portion is separated from the solid by means of a separatory funnel. The solid is discarded. The liquid amalgam is preserved under dilute sulfuric acid.

For the determination of titanium a sample equivalent to approximately 0.1 to 0.2 gram of titanium dioxide is digested with 20 cc. of concentrated sulfuric acid and 15 grams of powdered ammonium sulfate until it is entirely dissolved. Bulb *D* and the rubber tubing up through the stopcock are filled with the boiled water and both stopcocks are closed. Fifteen cubic centimeters of the zinc amalgam are added and the cooled sample is transferred to the funnel, using about 75 cc. of the distilled water. Two tablets of the sodium bicarbonate are now added and stopper *C* is inserted with cork *A* removed. When effervescence has ceased, two more tablets, broken into small pieces, are dropped through tube *B*. When the gas evolution is completed, cork *A* is immediately replaced and the entire apparatus vigorously shaken for 5 minutes.

The two stopcocks are now opened and the amalgam is allowed to flow into *D*. This displacement is best accomplished by alternately squeezing and releasing tube *E* with the fingers. As soon as the last particle of amalgam has dropped from the funnel, both stopcocks are closed and bulb *D* is removed for convenience while titrating. Stopper *A* is removed and 5 cc. of the potassium thiocyanate solution are added by means of a pipet through *B*. Stopper *C* is removed and both tube and stopper are washed into the funnel with distilled water. The solution is titrated in the funnel with the ferric ammonium sulfate. It is important that the ferric ammonium sulfate be added very rapidly until the first appearance of a wine-red color. The upper stopcock is now opened and tube *E* squeezed several times to force its liquid into the funnel. This will cause the wine color to disappear. The titration is completed by adding the ferric ammonium sulfate drop by drop to the end point.

Calcium sulfate, which is present in some commercial titanium pigments, does not interfere with the reduction because its precipitation is prevented by the high concentration of sulfuric acid. Barium sulfate should be removed by filtration before the reduction of the titanium.

Results

The pure titanium dioxide used in samples 1 and 2 was prepared in the laboratory of the Titanium Pigment Co., Inc.,

TABLE I. RESULTS OF ANALYSES

Sample	Weight of Sample Gram	Titanium ^a Di-oxide Present Gram	Titanium Di-oxide Found Gram	Error Gram
1	0.2000	0.2000	0.2006	+0.0006
2	0.2000	0.2000	0.2000	0.0000
3	0.2500	0.2470	0.2463	-0.0007
4	0.2500	0.2470	0.2470	0.0000
5	0.5000	0.1468	0.1459	-0.0009
6	0.5000	0.1468	0.1470	+0.0002
7	0.5000	0.1459	0.1448	-0.0011
8	0.5000	0.1459	0.1452	-0.0007
9	0.5000	0.1459	0.1458	-0.0001

^a Analyses by the Titanium Pigment Co., Inc.

by the method of Plechner and Jarmus (2). Samples 3 and 4 were Titanox A, a technical titanium dioxide pigment. Samples 5 to 9, inclusive, were Titanox C, which contains a large percentage of calcium sulfate. All the commercial

samples were analyzed in the aforementioned laboratories and the results were forwarded to the authors.

Acknowledgment

The authors wish to thank Joseph L. Turner, director of research of the Titanium Pigment Co., Inc., for the numerous analyzed samples contributed and for the private analytical methods of this corporation (3).

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Determination of Organic Sulfur by the Liquid Ammonia-Sodium Method

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CHABLAY (1) and later Vaughn and Nieuwland (3) showed that halogens were quantitatively removed as sodium halide from all types of organic compounds by the action of sodium in liquid ammonia. This reaction proved to be the basis of an excellent method for the quantitative determination of organic halogen.

The observation that certain organic sulfur compounds were decomposed by the action of sodium in liquid ammonia, led to the belief that sulfur in organic compounds might be reduced to sodium sulfide or sulfite by this method of treatment. If so, the resulting inorganic sulfur could be oxidized to sodium sulfate with the subsequent determination of sulfur by precipitation as barium sulfate. Such proved to be the case.

Kraus and White (2) studied the action of sodium in liquid ammonia on phenyl mustard oil, sodium benzene sulfonate, thiophenol, and diphenyl sulfide, and reported positive qualitative tests for sodium sulfite as a decomposition product of sodium benzene sulfonate. They also reported the formation of sodium sulfide in the decomposition of phenyl mustard oil and diphenyl sulfide. Williams and Gebauer-Fulnegg (4), however, have since shown that no sodium sulfide is formed in the case of organic sulfides, disulfides, and mercaptans.

Inasmuch as the success of this method depends upon the formation of sodium sulfide or sulfite, it is apparent that not all types of sulfur compounds can be analyzed by this method. Diphenyl sulfide and related compounds might, however, be analyzed by this method if they are first oxidized to sulfones, sulfoxides, etc.

Procedure

One-tenth gram of the material to be analyzed is placed in a 250-ml. beaker and approximately 175 ml. of liquid ammonia are added. If solution does not take place upon stirring, ether, monobutylamine, or other organic solvent inert towards sodium in liquid ammonia is slowly added until the sample is dissolved. Small pieces of freshly cut sodium are now added until a persistent blue solution of uniform depth is obtained. When the reaction is complete, the covered beaker is placed in a water bath at room temperature and the solution allowed to evaporate to approximately 25 ml. At this point 3 to 5 grams of ammonium chloride dissolved in a few milliliters of liquid ammonia are added to

destroy the excess sodium not utilized in the reaction. Evaporation is then continued to dryness.

The solids are dissolved in 75 ml. of hot water and 2 grams of sodium peroxide are added with stirring. The solution is heated to boiling, acidified with dilute hydrochloric acid, and heated vigorously for a few minutes to expel all traces of carbon dioxide and oxygen. A 5 per cent solution of barium chloride is then slowly added dropwise with constant stirring until the sulfate is completely precipitated. The precipitate is digested on a steam bath, filtered, washed, ignited, and weighed in the conventional manner.

The beaker containing the sample should be cooled by placing in a shallow dish containing about 0.5 cm. of liquid ammonia before the solvent ammonia is added. This avoids the violent spattering caused by the rapid vaporization of the ammonia on contact with the bottom of the beaker.

It has been found convenient at times to use a concentrated solution of sodium in liquid ammonia rather than finely cut pieces of metal. This modification is particularly useful when a large number of decompositions are being carried on at a single operation.

The use of organic solvents reduces the time of reaction and minimizes the possibility of error through incomplete decomposition.

Low results in analyses of compounds only slightly soluble in liquid ammonia or other solvents are partially remedied by the use of small samples and an excess of solvent. For example, by doubling the amount of solvent and reducing the size of the sample by one-half, the percentage of error in the determination of sulfur in thiourea was reduced from 1.3 to 0.26.

Results of analyses of sulfur compounds are given in Table I. All percentages are the average of at least two determinations.

TABLE I. ANALYSES OF SULFUR COMPOUNDS

Compound	Sulfur Calculated %	Sulfur Found %	Difference
Thiourea	42.12	42.01	0.11
Benzoyl sulfimide	17.48	17.35	0.13
Acetone diethyl sulfone	28.09	27.89	0.20
Dinitrophenylthiocyanate	14.24	13.49	0.75
Diphenyl sulfone	14.68	14.13	0.55
Benzenesulfonamide	20.41	20.51	0.10
Benzenesulfonyl chloride	18.16	18.07	0.09
<i>n</i> -Propyl- <i>p</i> -toluenesulfonate	14.97	14.83	0.14
<i>p</i> -Toluenesulfonic acid	16.86	16.45	0.41
2-Naphthylamine-5,7-disulfonic acid	16.81	16.27	0.54

TABLE II. AGREEMENT OF ANALYSES

Compound	Sample I	Sample II
Thiourea	41.96	42.05
Acetone diethyl sulfone	26.84	27.35
Dinitrophenylthiocyanate	13.48	13.50
Benzoyl sulfimide	17.31	17.39
Benzenesulfonamide	20.45	20.56
n-Propyl-p-toluenesulfonate	14.87	14.79

The agreement between duplicate analyses of the same sample of various sulfur compounds is shown in Table II.

Summary

A method has been outlined by which a large number of organic sulfur determinations can be carried on simultaneously and without the aid of special apparatus.

In those compounds which are soluble in liquid ammonia and do not form intermediate products which cannot be reduced to inorganic compounds, sulfur can be determined more quickly and just as accurately by this method as by the present lengthy bomb or fusion method.

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A Source of Loss of Ammonia in Kjeldahl Distillations

Method of Eliminating This Loss

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IN THE Kjeldahl distillation process, the first portions of ammonia liberated are so diluted with air as to escape complete absorption in the standard acid. This loss, generally overlooked, is appreciable and may easily be reduced by the use of a proper delivery tube. The purpose of this paper is to show the magnitude of the error and how to reduce it.

Moose (1) obviated the loss in the determination of ammonia in ammonium salts by suspending the salt in a small vial in the neck of a Kjeldahl flask and releasing the salt into the alkaline solution, after the solution started to boil. Though the accuracy of his results was one part per thousand, this procedure is not applicable to the usual Kjeldahl process.

The usual method of distillation is to make the sulfuric acid solution alkaline with a cold saturated solution of sodium hydroxide, pouring it carefully down the side of the flask so that it does not mix immediately with the acid solution, adding a few pieces of granulated zinc, pumice stone, or glass beads to prevent bumping. The distilling flask is then connected to a Hopkins distilling head which is in turn joined to a condenser, to which is attached a delivery tube dipping into standard sulfuric acid. The distillation is carried out slowly at first, the total time being about 1 hour.

In order to determine the loss of ammonia resulting from the usual method of distillation, a known solution of ammonium chloride was used.

Twenty-five cubic centimeters of an ammonium chloride solution equal to 42.55 mg. of ammonia (35.00 mg. of nitrogen) were pipetted into an 800-cc. Kjeldahl flask to which had been added some glass beads to prevent bumping upon subsequent distillation. Two hundred cubic centimeters of distilled water were added. Five cubic centimeters of a cold 41 per cent sodium hydroxide solution were carefully poured down the side of the flask, after which the flask was immediately attached to a Hopkins distilling head which by means of rubber tubing had been connected to a block-tin condenser. There was joined to the outlet of the condenser a delivery tube (a calcium chloride-type tube) which dipped under the surface of 50 cc. of standard sulfuric acid, contained in a 400-cc. beaker, into which the ammonia was distilled.

The distillation was carried out very slowly for the first 30 minutes, during which time about 15 cc. of distillate were obtained. The total time of distillation was 1.25 hours, at the end of which 175 cc. of solution had distilled over. The results

obtained from forty-seven 25-cc. samples of the ammonium chloride solution are given in Table I, and show a loss of 1.26 per cent of the total nitrogen, with a deviation from the experimental average of ± 1.24 per cent.

TABLE I. NITROGEN LOSS IN USUAL METHOD

Theoretical Nitrogen Mg.	Nitrogen Found Mg.	No. of Determinations	Deviation from Average Mg.
35.00	34.35	11	± 0.26
	34.58	11	± 0.27
	34.83	3	± 0.10
	34.37	11	± 0.62
	34.85	11	± 0.18
Av. 34.56 ± 0.43			

In order to show that this loss of nitrogen is due to the incomplete absorption of ammonia, at the beginning of the distillation, the 5 cc. of sodium hydroxide were suspended in the neck of the Kjeldahl flask by means of a small glass vial hung to a bent glass rod which led through the stopper of the Kjeldahl flask to the outside. After the ammonium chloride solution had been boiled to expulsion of the air, the vial of sodium hydroxide was released into the ammonium chloride solution. The distillation from this point onward was identical to that described for the determinations given in Table I. The average amount of nitrogen obtained from nine determinations was found to be 35.01 ± 0.01 mg. The average of these nine determinations is 0.03 per cent higher than the theoretical; the average deviation is ± 0.03 per cent, which may be considered as negligible.

Obviously this method of distilling off the ammonia cannot be applied to the sulfuric acid Kjeldahl solutions. As an alternative, it was thought that if the air bubbles were broken up by passing them through very minute openings, the ammonia which they contained would be absorbed by the standard sulfuric acid into which it is distilled. In order to ascertain whether or not the air bubbles could be broken up to such an extent as to prevent the loss of nitrogen from this source, the delivery end of the calcium chloride-type tube was closed and flattened. Ten holes, each 0.08 mm. in diameter, were made in the bottom of the tube. Eight distillations were carried out, except for this modification, identical with those described for the results obtained in Table I. The experimental average of these eight determinations is 34.99 ± 0.02

mg. This average is 0.03 per cent less than the theoretical; the average deviation from the mean average is ± 0.06 per cent.

In order to make this last procedure comparable to a regular Kjeldahl distillation, 20 cc. of concentrated sulfuric acid were added to the ammonium chloride solution plus 180 cc. of distilled water. Fifty-seven cubic centimeters of 41 per cent sodium hydroxide solution were carefully poured down the side of the flask and the distillation carried out as outlined in the previous procedure. The experimental average from eight determinations is 34.98 ± 0.04 mg. of nitrogen. This average is 0.06 per cent lower than the theoretical; the deviation from the mean average is ± 0.12 per cent.

Summary

Loss of ammonia by the usual Kjeldahl distillation procedure has been ascribed to the fact that some ammonia during the first few minutes of distillation is diluted with air to such

an extent that part of it escapes absorption by the standard sulfuric acid through which it passes.

The average loss of nitrogen resulting from forty-seven determinations with ammonium chloride solution has been shown to be 1.26 per cent, the average deviation being ± 1.24 per cent.

The usual Kjeldahl procedure has been improved by the use of a delivery tube containing holes, each 0.08 mm. in diameter, which cause the air bubbles resulting during the first few minutes of distillation to be broken up to such an extent that the average loss of nitrogen resulting from eight determinations is 0.06 per cent, with an average deviation of ± 0.12 per cent.

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A Rapid Method for the Volumetric Determination of Indium

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THE recent commercial availability of indium has revealed the need for rapid analytical methods for its determination. The method usually employed in commercial laboratories at the present time consists of precipitation of the indium as the hydroxide and ignition to the oxide (4). This procedure is unsatisfactory because of the unavoidable interference of iron, and because of the excessive time required for routine determinations.

A potentiometric method has been devised (1) using potassium ferrocyanide and the usual potentiometric equipment. This equipment is not always available in commercial laboratories.

The method to be described involves the titration of an indium acetate solution with potassium ferrocyanide in the presence of diphenylbenzidine as an internal oxidation-reduction indicator.

Reagents

Diphenylbenzidine, 2 grams in 100 cc. of concentrated sulfuric acid (sp. gr. 1.84).

Potassium fluoride, 10 grams of salt in 100 cc. of water.

Potassium ferrocyanide, 2.5 grams of trihydrate in a liter of water plus 0.2 gram of potassium ferricyanide.

The sulfuric acid used to make up the indicator solution should be free from nitrates and nitrites. Heating the acid until fumes of sulfur trioxide are evolved will eliminate these radicals.

Procedure

Weigh out a sample containing approximately 10 to 15 mg. of indium and dissolve in a suitable acid such as nitric acid or aqua regia. Remove the metals of Groups I and II with hydrogen sulfide. Make alkaline with ammonia in slight excess and digest on a steam bath or boil gently on a hot plate until faintly ammoniacal. Filter through a tight filter paper and wash sparingly with water.

Dissolve the precipitate in about 15 cc. of concentrated warm acetic acid (glacial) by repeatedly pouring the acid through the filter. Wash the filter with 10 additional cc. of the acetic acid and then with three 5-cc. portions of hot water, uniting both acid and washings. The resulting solution will contain both the indium and whatever iron is present as acetates.

If iron is present, as indicated by the tawny color of the hydroxides, add 0.5 gram of potassium fluoride dissolved in water as described above. The resulting solution should be about 60 per cent by volume of glacial acetic acid.

Cool the indium solution if necessary and add 2 drops of indicator. Titrate with standard ferrocyanide solution in a small cone flask, rotating the flask steadily until the end point is reached. The color change at the end point depends on the presence or absence of iron. If iron is absent and no fluoride has been added, the color change is sharp from slate blue to pea green which persists for 10 seconds with shaking. If iron is present and fluoride has been added, the end point is a sharp change from dull green to bright blue, the blue to persist for at least 10 seconds.

Discussion

One of the major applications of indium at the present is in dental gold alloys, which usually contain (in addition to indium) gold, silver, platinum metals, copper, and zinc. The indium can be separated from the other metals in such an alloy by means of a sulfide precipitation.

Dissolve the sample in aqua regia, add 5 to 10 cc. of sulfuric acid, take to fumes of sulfur trioxide, add enough hydrochloric acid to make about 1 *N* in total acidity (to prevent precipitation of indium sulfide), heat to boiling, and pass in a rapid stream of hydrogen sulfide for 30 minutes on a hot-plate. Filter off the sulfides without delay, boil the filtrate to expel hydrogen sulfide, and make slightly alkaline with ammonia. Digest, filter off the precipitated indium hydroxide, and treat as previously described. Acetic acid must be used to dissolve the precipitated hydroxide. For small percentages of indium no reprecipitation of the sulfides is necessary.

The potassium ferrocyanide solution is most conveniently standardized by titration against a solution of known indium content, best prepared by dissolving the pure metal in dilute nitric acid and proceeding as with an unknown sample. Should the supposedly pure indium contain tin, its presence will be indicated by a white residue insoluble in nitric acid.

The freshly precipitated indium hydroxide is very gelatinous and difficult to filter (5). Aging or digestion remedies this condition (2).

The sulfuric acid used to make the indicator solution should be fumed to sulfur trioxide to insure its being nitrite-free, as the presence of this ion causes a permanent blue in the indicator.

The titrating solution must be cooled to room temperature before the addition of the indicator (2).

TABLE I. RESULTS

Weight of Sample Grams	Indium Present Gram	Indium Found Gram	Error Gram
0.0226	0.0226	0.0224	-0.0002
0.0226	0.0226	0.0228	+0.0002
0.0452	0.0452	0.0449	-0.0003
0.0192	0.0192	0.0192	0.0000
0.0113	0.0113	0.0114	+0.0001
0.0141	0.0141	0.0142	+0.0001
0.0168	0.0168	0.0169	+0.0001
1.5047 ^a	0.0089	0.0089	0.0000
1.5970 ^a	0.0094	0.0091	-0.0003
1.5493 ^a	0.0090	0.0087	-0.0003

^a Dental gold alloys, C. A. Wamser, analyst, J. F. Jelenko & Co.

The end point cannot be obtained in the presence of chlorides.

If no fluorides have been added, the titrating solution should be made up to contain about 40 per cent by volume of glacial acetic acid. If fluoride is used, the final concentration should be about 60 per cent acid. The fluoride reduces the ferric-ion concentration by the formation of the complex $[\text{FeF}_6]^{-3}$ thereby preventing the formation of Prussian blue on the addition of potassium ferrocyanide. In this way the laborious separation of iron by 1-nitroso-2-naphthol (3) is entirely avoided.

The end point is not permanent, as in the case of the permanganate titration of iron in the presence of chloride ion, and it is therefore necessary to standardize the ferrocyanide under exactly the same conditions as prevail in the routine analysis.

This volumetric method requires considerably less time than the usual gravimetric analysis.

Acknowledgment

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Lignin in Douglas Fir

Composition of the Middle Lamella

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THE middle lamella has been subjected to extensive research, yet our knowledge of its structure and composition is far from complete. The exact relationship of this membrane to the various physical properties of wood is still a matter of conjecture. The nature of the so-called matrix surrounding each cell in wood is also an extremely important consideration in the impregnation of wood with preservatives. Furthermore, dissolution of the middle lamella is a goal of chemical pulping, yet even its approximate composition is unknown.

Previous Work

Initial investigations of the middle lamella were made by botanists who, on the basis of anabolic processes, stains, and solvents, concurred in the main in the belief that pectin or a derivative of it comprised most, if not all, of the middle lamella. This botanical concept was supported by the work of Frey, Treub, Strasburger, Mangin, Timberlake, Allen, and others (1) who relied largely on supposedly specific pectic stains and solvents. It was demonstrated that in certain tissues the middle lamella could be stained with ruthenium red or completely dissolved by pectic solvents; in nearly all tissue this staining effect was observed prior but not subsequent to treatment with a pectic solvent; hence, the conclusion that the middle lamella of most tissue was pectic. Botanists, however, studied tissues exceedingly diverse in kind, function, and age, and some recognized differences in the middle lamella which they attributed to differences in physical structure or chemical composition. While chemists, on the other hand, have disagreed almost unanimously with the botanical concept of the composition of the middle lamella, the two schools of thought were not always controverting the same thing, since studies by chemists were confined chiefly to mature xylem. As neither proponent completely or conclu-

sively disproved the other, it appears probable that both are partially correct. At any rate, each has made valuable contributions, while the controversy has stimulated progress. In view of the present knowledge of the combination and adsorption of stains, it seems probable that the early botanical investigators overestimated the significance of parallelism in staining effects, since Ritter, Harlow, Scarth, et al., demonstrated the unreliability of specific stains and solvents (10). These and other investigators found the lamella of mature xylem to be largely soluble in lignin solvents and insoluble in cellulosic solvents, to exhibit staining effects with supposedly specific lignin stains, and to possess optical properties attributive to lignin (2). Although the evidence in favor of chemists' conception of the composition of the lamella preponderates, there are no data indicative of the complete absence of pectic compounds or of an integral lignin content.

Experimental Procedure

In view of the fact that investigation of the middle lamella by the usual technic, *in situ*, did not make quantitative results possible, a method was developed to isolate mechanically a quantity sufficient for analysis.

With the aid of a micromanipulator of the Janse and Péterfi type (Figure 1), it was found possible to remove the lamella¹ in virtually a pure state. After experimenting with various types of glass microinstruments, a satisfactory tool was devised by grinding high-grade sewing needles to a chisel-like point on a silicon carbide stone, maintaining a constant grinding angle by mounting the needle in a small block of wood much as a blade is mounted in a carpenter's plane, and rotating the needle through

¹ Ritter's definition of the middle lamella (2), "the isotropic peripheral layer of cell wall, including the irregular masses of isotropic material commonly formed when three or more cells adjoin," describes the isolated material rather accurately.

180° when necessary to obtain equal grinding on each side, thus insuring the approximate equality of the length of the chisel edge and the diameter of the needle, as well as centration of the edge itself. The chisel was sharpened by the usual method of sharpening microtome knives, using the same block to maintain a constant sharpening angle. After mounting in a small wooden adapter which was then attached to the needle-holder of the micromanipulator, the needle could be actuated through the mechanism and made to perform exact and uniform movements in the three dimensions of space in its application to microscopic objects in the field of view of the microscope.

Various methods were tested, but it was found expedient to fasten sections to a slide by spreading a thin layer of an imbedding medium—of unusually desirable properties for this purpose, described elsewhere (3)—on the glass, allowing a tough film to form on the surface, and then pressing the section onto the layer of the imbedding agent. By mounting the slide on the mechanical stage of the microscope and simultaneously actuating the stage with one hand and the microtool with the other, it was possible to cut off fragments of the tissue, the size of which was limited only by the magnification, which, in turn, was limited by the working distance of the objective. By proper manipulation—i. e., moving the section of wood against the cutting tool by means of the mechanical stage, much as a log on a carriage is moved against a saw, with the section oriented so that only the tip of the knife could slide along the edge of a radial row of cells—it was possible to split off the outer radial row of cells, owing to a lack of cohesion in the middle lamella. The lamella itself was found to fracture approximately in the center, irregularly, or to tear loose from the adjacent secondary lamella; in the latter case the entire lamella adhered to one of the radial rows of cells.

This protruding material could be resected from the secondary wall (Figure 2) by moving the row of cells toward the vertical knife-edge and moving the knife nearer to or farther from the row of cells. The particles removed adhered to the knife, presumably because of static electrical charges, since the metallic knife was insulated by the wooden adapter. This permitted lifting the particles clear of the slide and inserting them, still on the knife, into the open end of a capillary tube mounted on the opposite standard of the micromanipulator. By discharging the knife or tapping it gently, the particles were dislodged and fell to the retaining capillary tube; the knife was removed—all the above operations being observed through the microscope—and the particles of lamella transferred to a microweighing bottle. The above disposition of instruments and use of the mechanisms of the mechanical stage and micromovements of the two standards had numerous advantages, foremost of which was the constant approximate centration of the knife in the field of view without additional adjustment.

To prevent inclusion of material other than the lamella, each particle was scrutinized for homogeneity. The middle lamella was found to be easily distinguishable from other lamellae by its dark finely granular appearance as contrasted with the almost colorless, crystal-like character of the remainder of the cell wall. Through the use of this technic on unstained and unextracted transverse sections of Douglas fir (*Pseudotsuga taxifolia*) heartwood, 200 microns thick, enough material consisting solely of the middle lamella was isolated from the summerwood to permit analysis. All resection was carried out under a magnification of approximately 100 diameters and grosser operations at a lower magnification. Material consisting of wood rays, summerwood, and springwood—the latter two containing the constituent ray tissue—was also isolated.

Samples of these tissues were analyzed for lignin by a micromethod developed by the author for the purpose (4).

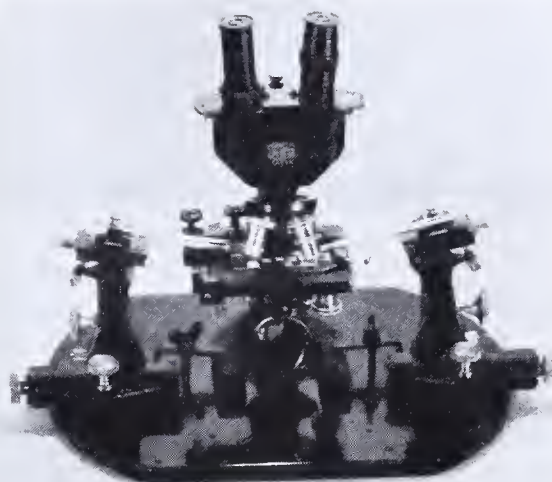


FIGURE 1. FRONT VIEW OF MICROMANIPULATOR AND BINOCULAR MICROSCOPE USED IN ISOLATION

Standard on right carries the needle-holder and microchisel; the other carries the glass capillary.

The sample of wood ray tissue was washed with hot alcohol-benzene solution prior to hydrolysis to remove resin; the other material was not extracted. In all the tissue analyzed, except the middle lamella, samples of approximately 3 mg. were used which was the size the author recommended for the microprocedure; only 0.5 mg. of middle lamella was available for analysis. The results of twenty-seven previous analyses (4) showed an extreme difference between highest and lowest values of 0.79 per cent with an average difference of 0.58 per cent, using samples of approximately 3 mg. This degree of precision probably obtains for the values obtained in the analysis of the wood rays, summerwood, and springwood, as the size of samples and analytical conditions were identical. In the case of the middle lamella, however, only 0.5 mg. of material was available for analysis. Since work of other investigators seemed to indicate that at least half of the middle lamella might be lignin, this quantity of material would yield 0.25 mg. of lignin, corresponding to a sample of wood of approximately 0.75 mg., or only one-fourth the size of sample which should have been used in microprocedure. As it was impractical to adapt the microprocedure to a smaller sample, preliminary analyses were carried out using samples of approximately 0.75 mg. to determine the error introduced by the use of the smaller sample. Four analyses showed an extreme difference between highest and lowest values of 1.56 per cent with an average difference of 1.21 per cent. The average lignin content obtained was 33.18 per cent, as compared with the earlier average of 33.41 per cent obtained on samples of approximately 3 mg. (4). This loss of precision was probably due to the approach to the sensitive limit of the balance (a Kuhlmann microbalance permitting weighing with a precision of ± 0.001 mg. with a maximum load of 20 grams on each pan) and to the solubility of the lignin, since the average yield of lignin is lower with the smaller samples.

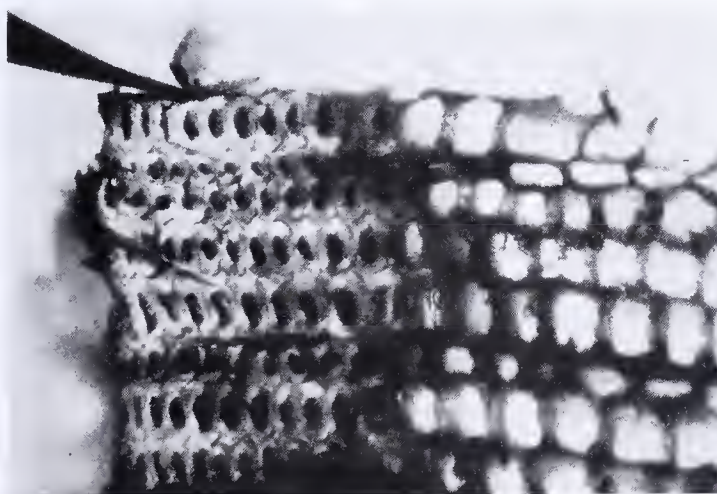


FIGURE 2. VIEW OF A SECTION ON A SLIDE

A radial row of cells has been split off, leaving most of the lamella adhering to the secondary wall of the exposed radial row of cells. The knife has resected part of the lamella. Section 200 μ thick; photographed in air without a cover glass. $\times 135$

Results

A single sample of middle lamella weighing 0.521 mg. was analyzed and the lignin content found to be 71.38 per cent. Samples of wood rays, springwood, and summerwood, weighing approximately 3 mg., gave values of 41.09, 35.24, and 31.56 per cent, respectively, all values being based upon the original oven-dry weight of the isolated material.

Discussion

There are no comparative quantitative data on the middle lamella. As the lignin content was found to be higher than the minimum assumed above, the precision is probably greater than was found to be the case with the 0.75-mg. sample. The amount of lignin isolated corresponded to a sample of wood slightly greater than 1 mg., or one-third the size of sample proposed for the microprocedure. Neglecting the effect of other variables, such as the effect of the dissolved carbohydrates, it would seem that the value of 71.38 per cent is susceptible to a maximum error of half of 1.39 per cent, which is the extreme difference between highest and lowest values which would be expected (assuming a direct relation between size of error and size of sample) with a sample of wood of approximately 1 mg. In other words, it seems probable that the lignin content of 71.38 per cent in the middle lamella isolated is not in error by more than 0.70 per cent of the true lignin content as measured by the microprocedure which was used in the analysis. In view of the fact that these experimental data must contain not only indeterminate errors—since there is no absolutely weight-constant receptacle, no absolutely insoluble compound, no absolutely pure precipitate or residue, and no absolutely accurate physical measurement—but also determinate errors, it seems valueless to apply statistical method in an attempt to determine deviation and error which, in this case, could have no significance. There was no evidence to indicate that the proportionately larger errors in balance reading, solubility and adsorption, etc., were not compensated sufficiently to permit the accuracy noted above.

Concerning the 28 per cent of the composition of the middle lamella left unaccounted for, part is probably due to the fact that, in spite of all precautions, the lamella isolated contained extraneous material. Each particle was examined minutely before it was accepted for analysis. In the author's opinion, the presence of 5 per cent of foreign material would probably be somewhat too high an estimate; in any case it is believed that it could not exceed 10 per cent. This would still leave some material unidentified. There is some evidence to indicate that the middle lamella contains hemicellulose as several investigators have suggested (7), which may account for the remainder of the lamellar substance.

Many botanists observed more or less definite layers in the middle lamella itself (discussed at length in Allen's paper, 1) and suggested (1) a splitting of the immature lamella with subsequent infiltration or excretion of other substance, (2) that the first thin layer of lamella decomposed during maturation of the entire lamella, or (3) in agreement with the later work of Harlow and Anderson that chemical metamorphosis of the lamella occurred, beginning at the secondary wall and proceeding toward the center of the lamella. Incomplete metamorphosis would then cause a layering effect. Anderson and Harlow considered this metamorphosis to be from a pectic compound to lignin. However, the pectin content of mature wood is very low. Pectin contains the radicals of araban and galactan derivatives, lignin and pectin are high in carbon and methyl content—recent findings indicate a high methyl content in hemicellulose (14)—pectin and lignin are associated with hemicellulose in plant tissue, and hemicellulose has been split from lignin (9) and from pectin. Con-

sequently, the suggestion that the central layer of the lamella may consist of hemicellulose which may be an intermediate product between pectin and lignin is perhaps worthy of more than casual consideration.

After removal of all lignin from wood chips by sulfite digestion, Klason noted that the dried chips were almost as stiff as the original wood, which effect he ascribed to residual hemicellulose (12). Klason's results were confirmed by the author (5) and similar effects noted earlier by delignification of wood by Ritter and Kurth, who also suggested hemicellulose in the middle lamella as the cause (14).

Carpenter and Lewis observed that the first effect of chemical digestion was a splitting of the middle lamella which left the fibers encased in the remains of the lamella, consisting largely of a spirally wound layer insoluble in cuprammonium solution and sulfuric acid (7), in rather striking agreement with the botanical conception of the double nature of the middle lamella. One hypothesis that might account for the initial splitting action of digestion is that the central layer of the middle lamella consists largely, if not completely, of hemicellulose which is hydrolyzed sooner or more easily than the lignin.

During the mechanical isolation of the lamella the author noted a definite tendency of the lamella to "cleave" either approximately in the center or at the union of the secondary wall, indicating a definite lack of cohesion in these points. When central cleavage occurred, it was frequently irregularly repand, serrate, or crenelated, the depths of the lacunae, however, being limited to a definite central zone. It was also frequently possible when the lamella was torn from the secondary wall to see very minute straplike elements on the edge of the lamella which had adjoined the secondary wall. These were probably fragments of the lamellar sheath of Carpenter and Lewis (7). Minute examination of the straplike elements showed them to have the same general appearance as the remainder of the lamella. Owing to the manner of isolation it was not possible to determine whether or not these elements had a spiral arrangement on the secondary wall. No confirmatory evidence was found regarding Lütke's claim that the middle lamella is many-layered (13).

Contrary to Forsaith (8), but in agreement with Harlow and Wise (11), the lignin content of wood rays was found to be considerably greater than in the total wood. This is supported further by the fact that wood rays have been shown to be sufficiently lignified to resist chemical digestion and beating and to appear intact in the finished sheet of paper (6).

The analyses of spring- and summerwood show about the same differences as do Ritter and Fleck's original values on the same wood (15). The most obvious explanation is that advanced by Allen and many others: that the lamella is of approximately the same absolute thickness in spring- and summerwood, but of smaller relative thickness in the summerwood.

Additional work is under way at the present time in an attempt to establish further the chemical composition of the middle lamella.

Acknowledgment

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Methods of Wine Analysis

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SAMPLING is more of a problem than one might suspect in an apparently homogeneous liquid such as wine. Air coming in contact with dry wine under certain conditions causes the formation of volatile organic acids. As this may occur at the top of a tank, the difference between the volatile acid content of the top and the bottom of a tank may amount to as much as 0.020 per cent. One tank was found to contain at the bottom, 0.108 per cent; middle, 0.125 per cent; and top, 0.148 per cent of volatile acid.

To secure a truly accurate sample, the entire tank should be thoroughly agitated; satisfactory results can usually be obtained by mixing samples from the top, middle, and bottom of the tank. For routine tests, a sample from the center of the tank will suffice.

ALCOHOL. Alcohol is usually determined in California wineries with the ebullioscope, but with the increasing number of chemists entering the wineries, the use of hydrometers and pycnometers is increasing. Some laboratories are increasing the accuracy of their ebullioscopes by determining the boiling point of wine distillates, but most plants still test the wine without this precaution. In the case of sweet wines, a dilution is sometimes made to reduce the effect of sugar on the boiling temperature. A limit of accuracy of 0.1 per cent is considered desirable.

Accurate alcohol spindles are now available at a reasonable figure and can be used in as little as 100 cc. A convenient method used in some plants is to distill 100 cc. of wine plus 50 to 75 cc. of water into a 100-cc. volumetric flask, and determine the alcohol on the distillate with a spindle. The residue in the boiling flask can be washed into a 100-cc. volumetric flask and the solids or "dry extract" roughly determined with a Balling hydrometer. This dealcoholized residue may be saved for the subsequent determination of reducing sugar and tannin.

VOLATILE ACIDS. This term is used to describe those substances removable from wine by steam distillation and possessing an acid reaction to phenolphthalein. In the United States volatile acids are calculated as acetic acid. With the recent introduction of new limits on volatile acids, this test becomes vitally important and greater accuracy in its determination is desired than previously, a limit of 0.005 per cent being frequently requested.

Slight variations of the official method (1) are in general use; usually a 10-cc. sample is steam-distilled until 50 to 100 cc. of distillate are collected, titrated, and calculated as acetic acids.

At present the various regulatory agencies, following the official method of the Association of Official Agricultural Chemists, do not make allowance for the fact that any sulfur dioxide in the wine is distilled and measured as a volatile acid. Certain types of wines (Haut Sauterne and Château Yquem) need up to 0.035 per cent of sulfur dioxide to prevent fermentation in the bottle. When titrated as a volatile acid, 0.035 per cent of sulfur dioxide is equivalent to 0.066 per cent of acetic acid. The limit on a white wine is 0.110 per cent of volatile acid as acetic; $0.110 - 0.066 = 0.044$ per cent of normal volatile acid, which might be taken as the limit for these types of wines. Such a limit excludes with certainty any wines over a year old.

TOTAL ACIDS. This is the term used to describe the total titratable acidity in wine. It includes both volatile and fixed acids and is calculated as tartaric acid. The determination of total acidity in white wine presents little difficulty when phenolphthalein is used as an inside indicator (1), but the intense red color of red wine makes the use of phenolphthalein as an inside indicator difficult unless diluted with 50 to 150 volumes of boiling distilled water.

Some chemists use a mixture of 1 per cent phenolphthalein powder in powdered potassium sulfate as an outside indicator. For rough work many chemists use the change in color of the natural anthocyanin pigment of the grape as an indicator. Absolute accuracy is not as important in this determination as some others.

REDUCING SUGARS. Reducing sugars are frequently determined by the Lane and Eynon method (3), which measures the amount of unused cupric ion after the wine has been boiled with a known amount of Fehling's solution. The official or Munson and Walker (5) method is not very popular among the wineries, because it is slow and requires an analytical balance. The Shaffer and Hartmann (8) method, a volumetric iodometric method, is being used in many plants where a high degree of accuracy is desired, and is popular in the various fruit industries in California. An accuracy of 0.010 or 0.020 per cent is desirable in the reducing sugar test.

METALS. Iron and other metals are to be avoided in wine because they form a recurring cloud and render the wine difficult to stabilize. The limits for iron and tin, the two worst metals in wine (7), are about 2 to 5 p. p. m. The method of Leavell and Ellis (4) is being used for the determination of iron with apparent satisfaction by several plants.

SULFUR DIOXIDE. Sulfur dioxide in wine is best determined by the bicarbonate-hydrochloric acid (6) method such as is in general use in the dried fruit industry. Satisfactory results may be obtained using a 32- or 50-cc. sample, distilling into iodine, and titrating with thiosulfate. The federal limit on sulfur dioxide in wines is 0.035 per cent and an accuracy of 0.005 per cent may be expected of the analyses.

TANNIN. Tannin in wines is usually considered of insufficient importance to warrant analysis. However, where desired, the official method (2), using indigo-carmin as an

indicator and titrating with standard permanganate, is followed.

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Micro-Dumas Generation of Carbon Dioxide

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WHILE the use of the Kipp generator as a source of carbon dioxide is satisfactory, this is true only when two generators are coupled in series.

A much simpler method is to generate the carbon dioxide from magnesite, contained in the closed end of the combustion tube. This method utilizes very little space, an item of consideration in most laboratories, and the cost of equipment is greatly reduced, the combustion tube and the microazotometer being all that is necessary in addition to the balance. Berl and Burkhardt (1) have described a semi-micromethod for the determination of nitrogen, using magnesite as the source of carbon dioxide and an average specimen of 30 to 40 mg. of substance. They use an azotometer with a graduated volume of 10 cc. (2).

In the present method an ordinary microcombustion tube is used, one end being sealed off and rounded, making a tube approximately 40 cm. long. Magnesite is introduced into the closed end of the tube to a depth of about 3 cm. It is necessary to use Kahlbaum magnesite (*für anal.*), the pea size being broken into smaller pieces. Following the magnesite in successive order are an asbestos wad of about 3 mm., 4 cm. of copper oxide, the specimen (3 to 4 mg.) mixed with copper oxide, copper oxide for about 5 cm., an asbestos wad, reduced copper spiral followed by asbestos, 5 cm. of copper oxide, and finally another asbestos wad, leaving about 5 cm. of the tube empty.

Before the combustion of the specimen, the tube is swept free from air by heating the magnesite. The closed end is surrounded with wire gauze, to eliminate distortion, and heated with a strong flame, and at the same time the long burner is turned on. Bubbles with a diameter of

one-tenth division appear in from 4 to 5 minutes, and true microbubbles are obtained if heating is continued for another minute. When bubbles of one-tenth division appear in the azotometer the flame under the magnesite is turned down until the barely luminous flame just touches the gauze, so that the generation of carbon dioxide is nearly stopped.

The combustion is carried out in the usual manner. The rate of decomposition of the compound can be controlled very accurately, as there is very little free space behind the specimen, and any change in the rate of decomposition is indicated immediately in the azotometer. When the specimen is completely decomposed and the burner under the specimen has reached the long burner, the flame under the magnesite is increased slowly until the nitrogen has been removed and the microbubbles appear in the azotometer. The writer uses two combustion tubes, one being filled while the other is in use.

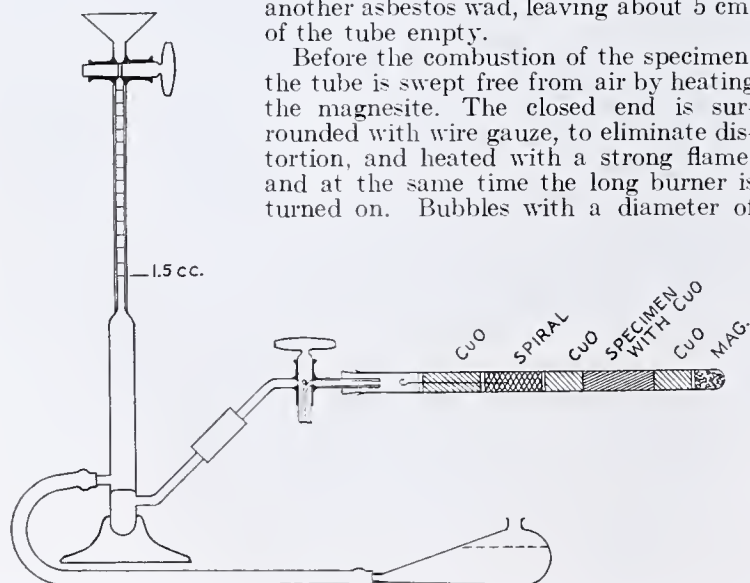
The decomposition of the specimen and sweeping of the gases take from 25 to 30 minutes, depending on the amount of nitrogen in the compound. The azotometer is read after 10 to 12 minutes. The total time from the beginning of sweeping until the final reading of the nitrogen volume should not exceed 50 minutes. From the volume of nitrogen collected, 2.2 per cent is deducted to give the net volume to be reduced to normal conditions. This value is determined by analyzing a known compound—for example, Kahlbaum hippuric acid—at the beginning and end of each series of analyses. This value has remained constant, and obviously represents a blanket correction, apart from temperature and pressure corrections. All the nitrogen values in the publications from this laboratory during the past three years have been determined by this procedure.

The method was investigated at the suggestion of J. S. Buck of this laboratory.

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Direct Simultaneous Microdetermination of Carbon, Hydrogen, and Oxygen

IV. Analysis of Bituminous Coals and Derived Products

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THE oxygen content of coal is generally calculated by difference—that is, the sum of the percentages of all directly determined elements is subtracted from one hundred and the difference is considered to be oxygen. In such a method, all the errors, cumulative or compensative, made in the individual determinations are included in the value assigned to oxygen. The importance of a direct method for the determination of oxygen in coal and its products has been stressed repeatedly (22). The purpose of this paper is to report the results obtained in the direct determination of carbon, hydrogen, and oxygen in various fuels using the gasometric microcombustion method which was developed in this laboratory on pure organic compounds (10, 11, 12).

Two methods have been suggested for the direct determination of oxygen in fuels. The hydrogenation method of ter Meulen and Heslinga (16) has been applied to the analysis of coal and its products by a number of investigators (1, 3, 15, 19). In a critical study of this method as applied to the analysis of coal, Schuster (19) pointed out that although it yields excellent results for oxygen in pure compounds, it is not faultless when applied to coal. This is due to the simultaneous hydrogenation of the mineral matter present in the coal sample. Besides Schuster's criticism, this method also possesses the disadvantage that in analyzing complex substances, such as fuels, the determination of the oxygen content of the sample becomes less simple, less direct, and hence less accurate the greater the number of elements present besides carbon, hydrogen, and oxygen. Also because of the deposition of carbon and poisoning by sulfur and halogens, the catalyst rapidly loses its activity and must be frequently renewed. An advantage of the method is that oxygen can be determined independently without the necessity of also determining other elements.

The gasometric combustion method has also been used for the direct determination of oxygen in various fuels (4, 5). Previous investigators using this method have assumed that the nitrogen present in the sample escaped completely in the elementary state and the sulfur was oxidized completely to sulfur dioxide or trioxide. A critical analysis of the results obtained with this method has revealed that they contain rather large compensative errors and that certain of the assumptions made are incapable of experimental confirmation. For this method to be successful when applied to fuels, much

This paper describes the application of a method for direct determination of oxygen, developed on pure compounds (10, 11, 12), to the complicated substances, coal and products derived from it. The previously described work on this general method of analysis showed that knowledge of the types of nitrogen linkage in the compound to be analyzed is necessary for exact computation of the oxygen content from the combustion data. When this knowledge is not available, as in the case of coal, the use of the present analytical method permits one to reverse the argument and draw conclusions regarding the type of nitrogen linkage predominantly present in the substance analyzed. In this respect the paper describes a method of analysis which may be used to determine not only elementary composition, but also, in part, chemical constitution. The fact that the application of this method to coal permits conclusions to be drawn regarding the type of the nitrogen linkage present emphasizes that the method has indirect as well as direct value.

greater accuracy must be attained in the carbon-hydrogen determination than has so far been reported because errors in the determination of these elements are multiplied by large factors in terms of oxygen. Likewise, the accuracy of the gasometric determination of "oxygen consumed" is capable of considerable improvement. Also, the fate of the nitrogen and sulfur must be determined so as to be able to correct the volume of oxygen consumed as well as to permit accurate calculation of the oxygen content of all of the combustion products. These details have been worked out in this laboratory using pure organic compounds, and the results have already been published (10, 11, 12).

Schuster (18) has also criticized this method from a theoretical standpoint. He asserts that "ash reactions" will likewise be involved, the most important being the splitting out of hydrate-water from silicates, evolution of carbon dioxide from inorganic carbonates, and the formation of sulfates, especially calcium sulfate. These reactions compensate to some extent, the first two tending to make the oxygen values high while the last tends to make them low. The net result, in the case of fuels in which sulfate formation is low, such as bituminous coals, would be to yield high results, while fuels in which sulfate formation is high, owing to a high content of calcium salts, as in brown coals, would tend to yield low results.

The particular advantage of this method is that carbon, hydrogen, and oxygen are determined simultaneously, and these, as well as moisture and ash, can be determined on a single weighed sample. Another advantage is that the presence of sulfur, halogens, and nitrogen has no harmful influence on the combustion tube filling and numerous series analyses can be made without changing the filling. A disadvantage is that in order to determine the oxygen content of a sample it is necessary to know the percentage of other elements (except halogens) present in the sample. For the purposes of this laboratory this is not a serious disadvantage since, in general, the complete composition of the sample is desired in order to make up elementary balances. The direct oxygen determination then serves as a control on all the other analyses made on the sample. The final advantage of this method when applied to microsamples is that it is essentially a modification of the Pregl carbon-hydrogen determination and Pregl's classical development of this method serves as the basis for the

procedure. In case of the hydrogenation method, much fundamental work must undoubtedly be done in order to convert it into a micromethod.

Experimental

The apparatus and procedure used in the analyses on coal and its products are identical to those used in the studies on pure organic compounds (10, 11, 12).

In the determination of the oxygen content of the fuel samples the hypotheses derived from the work on pure compounds were used. The nitrogen and sulfur in the fuels, determined by independent analyses, are considered, as a result of thermal decomposition, to be present in simple fragments which are then oxidized, under the conditions existing in the combustion tube, yielding only elementary nitrogen, nitrogen peroxide, and sulfur trioxide. As has been demonstrated (12) the ratio of nitrogen peroxide to nitrogen is a function of the type of nitrogen linkage present in the compound. In order to determine the oxygen content of the fuel samples, the type of nitrogen linkage present must be known.

Very little is known regarding the manner in which nitrogen is linked in coal and its derived products (17). Most authorities seem to agree that protein materials are the source of nitrogen in coal. According to Shacklock and Drakeley (20), the amount of nitrogen which can be extracted from fuels with 33 per cent sulfuric acid varies inversely with the rank of the fuel. Coalification appears to convert basic nitrogen compounds into substances of a neutral nature.

Terres (21) has pointed out that when bituminous coal is subjected to dry distillation the greatest part of the nitrogen (40 to 65 per cent) remains in the coke in a very thermostable form, 10 to 14 per cent evolves as ammonia, and the residue (21 to 50 per cent) is evolved as elementary nitrogen, cyanogen, or hydrogen cyanide or is present in the tar. Since some ammonia is obtained on dry distillation Terres concluded that probably all the nitrogen in the coal first appears as ammonia, the other nitrogen-containing substances being formed as a result of secondary reactions of the ammonia. Terres dry-distilled a variety of pure compounds at a temperature of 700° to 900° C., in an atmosphere of carbon dioxide, and found that only compounds containing amino or substituted amino groups were capable of yielding ammonia under these conditions and concluded that these groups must be present in coal.

However, it seems rather unlikely that any considerable number of such chemically active groups as amino or imino groups can be present in bituminous coal after having been subjected to as rigorous a reaction as coalification. The amino group is generally more reactive than the hydroxyl group, toward the same reagents, and bituminous coal is known to contain very few free hydroxyl groups even though the percentage of oxygen is much higher than the percentage of nitrogen. The hydroxyl number of coals also decreases regularly as the rank of the coal increases (?). It would seem more reasonable to believe that the nitrogen in coal is bound in a heterocyclic linkage as a result of condensation of amino or substituted amino groups with other reactive groups.

It is well known that on subjecting bituminous coal to low-temperature coking, high-temperature coking, and gasification processes, the amount of nitrogen in the residue decreases in the order named. The ammonia content of the gases from low-temperature coking is low, is high from high-temperature coking, and again low from gasification. The fact that any ammonia is obtained on gasification is due to the protection of the ammonia against further reaction by the presence of other gases and water vapor. Muhlert (17) states that in the absence of steam during gasification, the nitrogen compounds of coal, just as in combustion, yield no ammonia but are com-

pletely decomposed into elementary nitrogen. In a combustion analysis the coal is, in reality, subjected successively to all three of the above-named reactions. It is conceivable that during the first stages of the combustion some ammonia would be evolved according to Terres' idea, but here the ammonia is mixed with a huge excess of oxygen and is not protected from thermal decomposition and so would undergo this reaction as well as a high-temperature catalytic oxidation. In the final stage of the combustion the residual coke is gasified and in this stage only elementary nitrogen would be expected.

On the basis of the hypotheses advanced in connection with the study of pure nitrogen-containing compounds (12), if little or no hydrogen is attached to the nitrogen in the coal—that is, postulating that the nitrogen of the coal is predominantly present in a heterocyclic linkage—very little ammonia but rather cyanogen and perhaps hydrogen cyanide would be expected as a result of thermal decomposition and these, on oxidation, would yield nitrogen peroxide and nitrogen. The formation of ammonia could be explained, without assuming its direct evolution from the coal, by the reaction between the cyanogen and hydrogen cyanide with water vapor which is formed simultaneously. It is this type of reaction which is considered to occur when coke is treated with steam in order to improve the yield of ammonia, the coke nitrogen being practically quantitatively converted into ammonia (2, 21), and is the basis of the Mond process.

Although the heterocyclic linkage of nitrogen in coal is preferred, and since the type of linkage is not definitely known, it was decided to calculate the percentage of oxygen present on the assumption that (1) the nitrogen is present as heterocyclic nitrogen (method 1 in the tables), and (2) the nitrogen is present in amino or amido groups (method 2 in the tables). From the work on pure nitrogen-containing compounds (12), it was found that the first-mentioned type gave satisfactory results for oxygen when it was postulated that 59 per cent of the nitrogen was converted to nitrogen peroxide and 41 per cent to nitrogen. The second types gave satisfactory results for oxygen when it was postulated that 26 per cent of the nitrogen was converted to nitrogen peroxide and 74 per cent to nitrogen.

Table I gives the results obtained on a bituminous coal A, Table II on Edenborn coal, which is being intensively studied in this laboratory, and Table III on the residue remaining after Edenborn coal had been subjected to the action of 5 *N* sodium hydroxide solution for 24 hours at 300° C. Unless otherwise noted, the analyses were performed in the Coal Research Laboratory on microsamples. In accordance with the results obtained on pure sulfur-containing compounds (11), all the calculations include the complete oxidation of the sulfur present in the sample to sulfur trioxide, followed by absorption as silver sulfate, one atom of oxygen being consumed in the last reaction for each atom of sulfur present.

In Tables I, II, and III on the basis of the first assumption, the directly determined oxygen is, with two exceptions, higher than oxygen calculated by difference and the sum of all directly determined constituents approximates, but averages slightly greater than 100 per cent. On the basis of the second assumption, the directly determined oxygen is, in every case, lower than oxygen calculated by difference and the sum of all directly determined constituents falls considerably short of 100 per cent. The data in Table II also indicate the slow oxidation which the Edenborn coal has been undergoing during storage. Both the oxygen determined directly and that calculated by difference show that the sample stored in glass in 1931 had oxidized to a smaller extent than a sample which had been stored in a large steel drum.

These data on coals appear to confirm the theoretical deductions of Schuster (18) regarding the absolute magnitude

TABLE I. COAL SAMPLE A

Weight of Sample	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen		Sum of Directly Determined Constituents	
	C	H	N	S	Ash	C	H		Method 1	Method 2	Method 1	Method 2
	Mg. %	%	%	%	%	%	%	%	%	%	%	%
6.554 ^a	82.18	4.62	1.24	0.57	6.42	87.83	4.94	4.97	5.14	3.74	100.17	98.77
7.496 ^a	82.03	4.68	1.24	0.57	6.78	87.99	5.01	4.70	4.67	3.27	99.97	98.57
6.986 ^a	82.92	4.64	1.24	0.57	5.67	87.90	4.92	4.96	4.40	2.99	99.44	98.03
6.792 ^a	82.79	4.68	1.24	0.57	5.73	87.82	4.96	4.99	5.52	4.11	100.53	99.12
7.300 ^a	82.22	4.68	1.24	0.57	6.21	87.65	4.99	5.08	5.60	4.21	100.52	99.13
Mean	82.43	4.66	1.24	0.57	6.16	87.84	4.96	4.94	5.07	3.66
^b	83.09	4.70	1.28	0.57	5.91	88.31	5.00	4.45
^c	83.39	4.79	1.21	0.57	5.59	88.33	5.07	4.45

^a Analyzed November, 1934.
^b Analyzed October, 1933, by Laboratory A.
^c Analyzed May, 1934; mean of two determinations.

TABLE II. APPARENT ATMOSPHERIC OXIDATION OF EDENBORN COAL SAMPLES IN STORAGE

Weight of Sample	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen		Sum of Directly Determined Constituents	
	C	H	N	S	Ash	C	H		Method 1	Method 2	Method 1	Method 2
	Mg. %	%	%	%	%	%	%	%	%	%	%	%
^a	79.0	5.1	1.6	1.0	7.6	85.5	5.5	5.7
^b	78.27	5.26	1.62	0.98	8.39	85.44	5.74	5.48
^c	78.07	5.21	1.66	0.95	7.98	84.84	5.66	6.13
^d	77.92	5.15	1.66	0.96	7.90	84.60	5.59	6.41
6.906 ^e	77.54	5.27	1.52	1.00	7.96	84.26	5.72	6.71	7.50	5.78	100.79	99.07
7.614 ^e	77.41	5.14	1.52	1.00	7.96	84.10	5.58	6.97	7.33	5.62	100.36	98.65
7.389 ^e	77.79	5.15	1.52	1.00	7.96	84.52	5.60	6.58	7.27	5.58	100.69	99.00
7.597 ^f	78.32	5.09	1.65	1.00	8.00	85.13	5.53	5.94	7.02	5.15	101.08	99.21
7.376 ^f	78.27	5.06	1.65	1.00	8.07	85.14	5.51	5.95	6.77	4.89	100.82	98.94

^a Analyzed September, 1931 [*Bur. Mines Tech. Paper 525* (1932)].
^b Analyzed February, 1933.
^c Analyzed May, 1934, by Laboratory A.
^d Analyzed July, 1934, by Laboratory A.
^e Analyzed December, 1934.
^f Analyzed February, 1935. Sample ground and sealed (with paraffin) in glass bottles in June, 1931. Air displaced by natural gas.

TABLE III. ALKALI-TREATED EDENBORN COAL RESIDUE

Weight of Sample	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen		Sum of Directly Determined Constituents	
	C	H	N	S	Ash	C	H		Method 1	Method 2	Method 1	Method 2
	Mg. %	%	%	%	%	%	%	%	%	%	%	%
6.636 ^a	84.77	5.28	1.62	0.33	2.19	86.66	5.40	5.81	6.36	4.52	100.55	98.71
7.728 ^a	84.86	5.28	1.62	0.33	2.23	86.79	5.40	5.68	6.39	4.56	100.71	98.88
Mean	84.82	5.28	1.62	0.33	2.21	86.73	5.40	5.75	6.38	4.54
^b	85.30	5.41	1.62	0.33	2.12	87.15	5.53	5.22

^a Analyzed December, 1934.
^b Analyzed October, 1934.

of the values for oxygen as obtained by these methods. However, work on pure compounds has shown that the carbon-hydrogen determination is rarely perfect, the general tendency in this direct method being to yield slightly high values, especially for hydrogen. Since any error in hydrogen is multiplied by a rather large factor, the values obtained for oxygen tend to be high by about +0.3 per cent. In fact, direct determinations for carbon, hydrogen, and oxygen were made on samples of benzoic acid for the purpose of control, one just before the series of coal analyses and one just after. The direct oxygen values obtained in these determinations were high by +0.32 and +0.34 per cent, respectively. On this basis, using the sum of all directly determined constituents as a criterion, the value for oxygen which yields a sum slightly greater than 100 per cent would be preferred. Such values were obtained only when using the ratio of 59 per cent nitrogen peroxide to 41 per cent nitrogen. This is considered to offer strong support to the idea that by far the greatest part of the nitrogen in coal is present in some form other than amino or amido groups and it is suggested that the most likely form would be that of a heterocyclic linkage. In connection with the analyses made on the residue from alkali-treated Edenborn coal (Table III) it should be pointed out that any amide linkages, if present, would very likely be hydrolyzed under such drastic hydrolytic conditions. However, the nitrogen

content of this residue is practically the same as that of the original coal and only a faint odor of ammonia was noticed on opening the bomb after completion of the reaction. This evidence would also indicate the absence of amido groups in the coal and justify the use of the ratio of 59 per cent nitrogen peroxide to 41 per cent nitrogen in the calculations. In order to determine the magnitude of the error introduced by the so-called "ash reactions" mentioned by Schuster, a calculation was made using the combustion data obtained in the first December, 1934, analysis on Edenborn coal. The composition of the ash from this coal is available (6) and was used in calculating the mineral matter present in the sample (9). The oxygen content of the "hydrate-water" liberated from the various hypothetical hydrates as well as the oxygen content of the carbon dioxide liberated from hypothetical carbonates, is deducted from the previously used value for the oxygen present in the combustion products. The amount of "oxygen consumed" in oxidizing hypothetical lower oxides and sulfides to ferric oxide is also calculated and subtracted from the previously determined value for oxygen consumed. The formation of sulfates is not considered since, in this coal, the percentage of volatile sulfur is practically identical to the total sulfur. If the correction which results from these calculations is used, the value for the oxygen present in the sample is lowered by 0.53 per cent, so that, on the basis of 26 per cent

TABLE IV. STANDARD NITRO HUMIC ACID

Weight of Sample Mg.	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen		Sum of Directly Determined Constituents	
	C %	H %	N %	S %	Ash %	C %	H %		Method 1 %	Method 2 %	Method 1 %	Method 2 %
8.792 ^a	64.35	2.76	4.28	0.66	1.00	65.00	2.79	26.95	32.38	27.54	105.43	100.59
8.708 ^a	64.44	2.70	4.28	0.66	1.11	65.17	2.74	26.81	31.95	27.09	105.14	100.28
Mean	64.40	2.73	4.28	0.66	1.06	65.09	2.77	26.87	32.17	27.32
^b	64.52	2.73	4.21	0.67	1.19	65.30	2.76	26.68

^a Analyzed December, 1934.^b Analyzed October, 1934.

TABLE V. COKE SAMPLE A

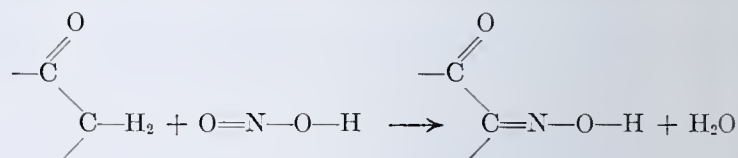
Weight of Sample Mg.	Moisture-Free					Moisture- and Ash-Free		Oxygen by Difference Moisture-Free	Direct Oxygen			Sum of Directly Determined Constituents		
	C %	H %	N %	S %	Ash %	C %	H %		Method 1 %	Method 2 %	Method 3 %	Method 1 %	Method 2 %	Method 3 %
6.318 ^a	89.96	0.54	0.86	0.50	7.72	97.50	0.59	0.42	1.61	0.65	-0.11	101.19	100.23	99.47
7.257 ^a	89.59	0.59	0.86	0.50	8.01	97.39	0.64	0.45	2.16	1.17	+0.41	101.71	100.72	99.96
Mean	89.78	0.57	0.86	0.50	7.87	97.45	0.62	0.44	1.89	0.91	+0.15
^b	90.27	0.54	0.89	0.57	7.43	97.52	0.58	0.30
^c	89.68	0.65	0.86	0.50	7.57	97.03	0.70	0.74

^a Analyzed December, 1934.^b Analyzed October, 1933, by Laboratory A.^c Analyzed May, 1934; mean of two determinations.

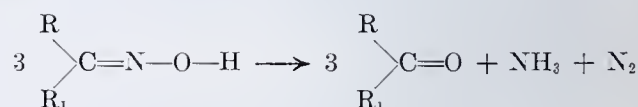
nitrogen peroxide to 74 per cent nitrogen it becomes 5.24 per cent and on the basis of 59 per cent nitrogen peroxide to 41 per cent nitrogen, 6.97 per cent. The latter, preferred value now agrees fairly satisfactorily with the oxygen calculated by difference but is still slightly higher. The sum of all directly determined constituents becomes 98.53 and 100.26 per cent, respectively. This indicates even more clearly the likelihood of the nitrogen in the coal being present as a heterocyclic or similar linkage. The deviation of the sum of the constituents from 100 per cent in the last case cited is practically identical to the deviations of the control analyses in which benzoic acid was used.

Two analyses were made of a "nitro" humic acid prepared by boiling Edenborn coal with *N* nitric acid for one week. This treatment increased the nitrogen content from 1.52 to 4.28 per cent. Such a reaction involves fairly drastic hydrolysis and it is doubtful if any amide groups could survive. Calculating the results on the basis of 59 per cent nitrogen peroxide formation (method 1) gave, in this case, the unreasonable total of 105.43 and 105.14 per cent for the sum of directly determined constituents. When calculated on the basis of 26 per cent nitrogen peroxide formation (method 2), the sum of directly determined constituents was 100.59 and 100.28 per cent. Since the oxygen values for the original coal were satisfactory when calculated by method 1 and unsatisfactory when calculated by method 2, it was anticipated that method 1 would also yield satisfactory results for the nitro humic acid. However, as indicated above, the reverse is true. As observed from a comparison of the elementary analyses of the original coal and the nitro humic acid, the nitric acid treatment reduced the carbon content from 78 to 64 per cent, the hydrogen from 5.2 to 2.7 per cent, and the ash from 8 to 1 per cent, and increased the nitrogen from 1.5 to 4.3 per cent. Aside from these changes, one would hardly expect such a deep seated change in the "nucleus" of the original coal as to invalidate the method of calculation which yielded satisfactory oxygen values for the original coal, nor would one expect any extensive change in type of the nitrogen linkage of the nitrogen present in the original coal, such as conversion from heterocyclic to amino or amido linkages.

How can this apparent anomaly be explained? According to Fuchs (8), when coal is heated with nitric acid the coal is oxidized and the nitric acid is reduced to nitrous acid. The latter reacts with active methylene groups in the coal forming isonitroso ketones:



On combustion, the fate of the nitrogen in an isonitroso ketone will depend, according to the hypotheses previously mentioned, upon what happens on pyrolysis and subsequent oxidation of the pyrolytic products. In a study of the action of heat on ketoximes, which are closely related, structurally, to isonitroso ketones, Kötze and Wunstorf (13) found that certain of these substances, in an atmosphere of carbon dioxide and at temperatures as low as 170° C., react practically quantitatively:



If it is assumed that the original nitrogen present in the coal is not affected by the nitric acid treatment, then 35.5 per cent of the total nitrogen in the nitro humic acids, on thermal decomposition and oxidation would be transformed into nitrogen peroxide and nitrogen in the ratio 59 to 41. The balance of the nitrogen, according to the above equation, would be converted into ammonia and nitrogen in the ratio 33.3 to 66.7. This ammonia would then be oxidized to nitrogen peroxide and nitrogen in the ratio 26 to 74. The net result of this series of reactions would yield, by calculation, 26.5 per cent of the nitrogen as nitrogen peroxide and 73.5 per cent as elementary nitrogen, which is approximately the ratio which was found to yield satisfactory results for oxygen in this sample. This agreement would appear to explain the anomaly mentioned above and also justify the use of the ratio of 26 per cent nitrogen peroxide to 74 per cent nitrogen for this particular substance and also confirm Fuchs's idea that the nitrogen, added to coal on treatment with nitric acid, is present in the form of an isonitroso ketone linkage. The data are summarized in Table IV.

Finally, two analyses were made on a sample of coke. The results are given in Table V. When calculated on the basis of 59 per cent nitrogen peroxide to 41 per cent nitrogen, the sum of all directly determined constituents is 101.19 and 101.71 per cent, whereas, when calculated on the basis of 26 per cent nitrogen peroxide to 74 per cent nitrogen, the sum is 100.23

and 100.72 per cent, which, as in the case of the original coal, appears to be a more reasonable figure.

According to Muhlert (17), gasification of coke in the absence of steam yields no ammonia, the nitrogen present being evolved, as in combustion, exclusively as elementary nitrogen. In the present work the combustion was conducted in an atmosphere of dry oxygen, and since coke contains a very low percentage of hydrogen there is little opportunity for steam formation. Muhlert also points out that the hydrogen in coke does not take part in the formation of ammonia during gasification. Van der Ley and Wibaut (14) likewise state that thermal decomposition of the carbon-nitrogen complex in coke prepared from coal begins at about 800° C. and is still slow at 1000° C., the nitrogen being split out solely in the elementary form.

On the basis of this information calculations were made assuming that all of the nitrogen of the coke was evolved as elementary nitrogen (method 3, Table V). The direct oxygen values obtained were -0.11 and +0.41 per cent, the sum of all directly determined constituents being, respectively, 99.47 and 99.96 per cent. While, in general, summations of over 100 per cent are preferred, because of the tendency of this method to yield high results, it is possible in this case that they are low because of the fact that the nitrogen values for the coke, determined by the micro-Kjeldahl method, are probably low. The oxygen values, calculated on the assumption that the nitrogen of the coke is all evolved as elementary nitrogen, are lower than those calculated on the other bases and also lower than those calculated by difference, which is, perhaps, the direction which many fuel chemists feel the oxygen values in coke should tend.

Summary

The gasometric microcombustion method for the direct determination of carbon, hydrogen, and oxygen has been applied to the analysis of two samples of bituminous coal as well as to an alkali-treated coal residue, a nitro humic acid, and a coke all derived from a bituminous coal.

With the knowledge available from the work on pure nitrogen-containing compounds (12), this method not only directly determines the oxygen content of fuels, but also enables certain deductions to be drawn as to the probable type of nitrogen linkage present in the various fuels analyzed. From the results obtained it is indicated that the nitrogen present in

bituminous coal exists in some linkage other than that of an amino or amido group, a heterocyclic linkage being preferred. In the case of the nitro humic acid, evidence is given which confirms the idea that treatment of a bituminous coal with nitric acid introduces nitrogen in the form of an isonitroso ketone linkage. In the case of coke the best results for oxygen are obtained on the assumption that all the nitrogen is evolved, during combustion, in the elementary state.

The preferred, directly determined oxygen values are, with the exception of those obtained in the coke analyses, higher than the values obtained for oxygen when calculated by difference. In the case of coke, the preferred direct results for oxygen are lower than those calculated by difference.

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A Precision Pycnometer for Liquids

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DURING some work on the concentration and reactions of heavy water, it was necessary to follow changes in composition by density measurements. Since numerous determinations were to be made and very slight changes in density detected, the method had to be both simple and accurate. Several common types of laboratory pycnometers were tried, but the results were not very satisfactory. The chief faults found were difficulty of thermostating both the liquid and container, evaporation losses at ground-glass joints, loss of liquid during filling (very important in handling expensive liquids), and difficulty of determining the density at some definite temperature.

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After preliminary work, the pycnometer shown in Figure 1 was evolved, and is believed to eliminate the faults enumerated above. It is 16.25 cm. (6.5 inches) long with capillary tubing having an outside diameter of 4 mm. and an inside diameter of 0.75 mm. The size of the bulb is limited by the size of the sample available or the accuracy desired. Sizes from 0.1 to 25 cc. have been used.

The liquid reservoir should be a test tube long enough to allow the pycnometer with cap removed to touch the bottom and with just enough clearance at the top to allow the stopcock to turn. The diameter of this tube should be such that no partial vacuum is created when the filled pycnometer is removed. Too close a fit will cause some of the contents to be removed. A thin rubber stopper which has been slit from the



FIGURE 1

periphery to the center will serve very well as a stopper for the ensemble. It should contain a tiny hole to admit air during the filling.

After thorough cleansing with acid dichromate, the stopcock should be greased on the inner part only. Since the pycnometer is wiped after handling, any weight lost due to the removal of stopcock lubricant would introduce an error.

The test-tube reservoir should contain slightly more liquid than is necessary to fill the pycnometer. If more than this is used, the pycnometer contents will be under a slight hydrostatic back pressure which when removed will cause the liquid level to fall below the mark. It is therefore well to have a mark on the test tube to indicate the proper liquid level.

In determining the density of a liquid, the procedure was as follows:

With the liquid up to the mark in the test-tube reservoir, the pycnometer without its cap was carefully inserted and the rubber stopper set in place. This ensemble was clamped into a glass-walled thermostat with the lip of the test tube only a short distance from the surface of the thermostat water, and allowed to come to thermal equilibrium (about an hour).

A rubber tube was connected to the stopcock, which in turn was connected to a three-way stopcock, a 100-cc. reservoir (to prevent any water from the leveling bulb from draining into the pycnometer), and a leveling bulb filled with water. The pycnometer stopcock was opened and the three-way stopcock adjusted so that water could be drawn up into the bulb. When the water was almost up to the upper capillary, the three-way stopcock was turned to allow the leveling bulb to make the careful final adjustment. Great care must be used in bringing the liquid up to the mark, as capillary action tends to draw it up. A screw arrangement on the leveling bulb will help this. The greatest accuracy is attained if the meniscus is brought up to the mark and the pycnometer stopcock closed, instead of going past the mark and then bringing it back.

With the pycnometer filled to the mark, it was removed from the test tube, the stopper removed, quickly wiped with a downward sweep of a towel, and the ground-glass cap placed on it. The rest of the pycnometer was then wiped. It was suspended in the balance in a vertical position by means of a small stirrup which hooked around the stopcock. After remaining in the balance for a standardized period of time, the weight was taken.

Under carefully controlled conditions and using a good analytical balance, it was possible to check weights to 0.1 mg.

The pycnometer has the disadvantage that, in working with a liquid having a high vapor pressure at room temperature, the interval between filling and weighing must be short, as the vapor pressure of the liquid tends to force it slowly out of the pycnometer. This might be overcome by placing the small opening in the cap nearer the ground-glass joint and allowing the liquid to drip into the cap during a weighing.

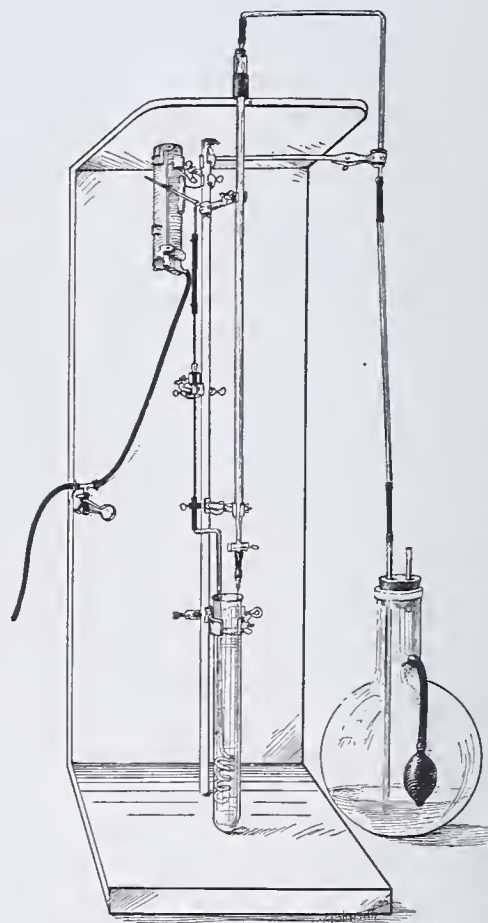
RECEIVED October 28, 1935.

ZINC PIGMENTS IN PAPER AFFECT ALPHA CELLULOSE, COPPER NUMBER, AND ACIDITY TESTS. Consideration of fiber purity in terms of alpha cellulose content and copper number has been recommended by the National Bureau of Standards in choosing record papers that are required to have a long life. It has been found, however, that when papers contain zinc pigments, the test values obtained by the present methods are affected. P. F. Wehmer, chairman of the TAPPI Subcommittee on Chemical Methods for Paper Testing has reported that amounts of zinc sulfide commonly used in papers appreciably increase the test values for both alpha cellulose and copper number. Furthermore, that the total acidity value, obtained by titration of an aqueous extract of the paper, is reduced. Until modified testing procedures can be developed to avoid the errors caused by the zinc pigments, the probable stability of papers containing them must be judged in some other way. Another criterion recommended is the amount of folding endurance retained by paper on heating it.

An Apparatus for Sugar and Other Titrations

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FOR a number of years the writer has been using a titration apparatus in sugar determinations which has made the work a great deal easier and also improved the accuracy. Because of the interest shown in the apparatus by workers who have seen and used it, an illustration and brief description of it is given.

As shown in the figure, a vacuum windshield motor (which may be of any good type) is connected by a side arm (6.25 cm., 2.5 inches long) to a vertical metal shaft (0.47 × 26.25 cm.,

0.1875 × 10.5 inches) by means of a small coil spring. The shaft runs through a short glass-tube bearing. The lower end of the shaft is attached to the glass stirring rod by a short piece of pure gum tubing. The 25-cc. buret (preferably graduated in 0.05-cc. intervals) is fitted with a 20-gage stainless-steel hypodermic needle (cut to 2.5 cm., 1 inch, length) by means of a piece of pure gum tubing. The writer cuts the tip of the buret to fit snugly into the hub of the needle. The buret is fitted with a siphon automatic leveling device by fastening a glass tube, with vent hole, over the top through which passes a tube into the buret. The tip of the tube should be constricted and preferably ground. It is placed so that when the titrating solution is pumped into the buret above the zero mark and the pressure released in the flask, the solution is siphoned to the zero mark on the buret. The leveling device should be well supported.

The glass stirring rod should extend almost to the bottom of the sugar tube on the down stroke. Either a loop or spiral rod is satisfactory, the spiral type being somewhat preferable. The buret, stirring rod, and sugar tube are placed so that the tube can be easily slipped into or out of the clamp when the stirring rod is raised.

The vacuum motor may be driven by a good water pump or other suitable source of vacuum and the speed of stirring controlled by inserting a T-tube and screw clamp in the vacuum line.

The 20-gage needle tip delivers about 0.008 cc. of aqueous solution per drop and insures good buret drainage and accurate end points.

The apparatus obviously may be used for many different kinds of titrations, though acid solutions should not be passed through the needle tip. A glass tip with fine point may be substituted for the metal tip when acid solutions are used.

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Detection and Separation of Difficultly Soluble Compounds by Concentrated Hydriodic Acid

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A BRIEF note published by the senior author (2) indicated that concentrated hydriodic acid should be a general reagent of considerable value for the analytical treatment of compounds of low solubility. It is especially useful for the examination of compounds unattacked by hydrochloric acid, nitric acid, or aqua regia, for their detection or separation may be more conveniently accomplished in many cases by the use of hydriodic acid than by the fusion processes and special methods usually employed. Since most of these new methods require but small quantities of hydriodic acid, and since much time can often be saved by its use, its comparatively high cost is not a serious objection. In this paper are reported the results of systematic analytical experiments with the following difficultly soluble compounds of common elements: stannic oxide, aluminum oxide, chromic oxide, silicon dioxide, barium sulfate, strontium sulfate, calcium sulfate, lead sulfate, chromic dihydroheptasulfate, silver iodide, silver bromide, silver chloride, calcium fluoride, and anhydrous chromic chloride.

Preparation of Materials

In the majority of the experiments Merck's ordinary grade of hydriodic acid of specific gravity 1.70 was used. This not only gives the same general results as the pure acid, but, as it is stabilized by the addition of 1 to 2 per cent by volume of 50 per cent hypophosphorous acid, is actually superior to the pure acid for certain qualitative tests, because the reactions are not obscured by the liberation of free iodine. For certain experiments, however, a highly pure acid of similar concentration was used, this being prepared either by passing hydrogen sulfide into a water suspension of iodine or synthetically by using a modification of the contact process of Bodenstein (1).

The various difficultly soluble compounds were especially prepared for the experiments by methods that yielded highly pure products.

General Qualitative Technic

Samples carefully weighed on an assay balance were employed in the test, particular attention being paid to the lower limit of observable reaction in order to determine the practical sensitivity for each substance. Small Pyrex test tubes were used for holding samples, since 2 to 3 ml. of acid were ample for exhibiting the characteristic reactions. In the case of compounds unattacked in the cold, the tubes were partially immersed in a beaker containing colorless mineral oil, so that the reaction mixtures could be heated to definite temperatures. In the experiments with the sulfates, lead acetate paper or

Concentrated hydriodic acid is a valuable general reagent for the detection and separation of compounds that are insoluble in hydrochloric acid, nitric acid, or aqua regia. It not only reacts in a distinctive manner with most of the individual compounds, but mixtures can be analyzed qualitatively by its use, and certain pairs or groups of insolubles can be separated quantitatively. Analytical procedures based upon the use of this acid are frequently much more rapid and convenient than the fusion processes usually employed. The relatively high cost of this reagent is not such a serious objection as it may seem, for the methods usually require small volumes of hydriodic acid and the time saved by its use often more than offsets the expense of the acid.

paper dipped into an ammoniacal solution of sodium nitroprusside was used in testing for the evolution of hydrogen sulfide. After decomposition of the samples by acid treatment, appropriate tests were made for the ions present in the resulting solutions.

Qualitative Behavior of Individual Compounds

As stated previously (3), stannic oxide is not noticeably attacked by concentrated hydriodic acid in the cold, but at temperatures of 90° to 95° C. and above the compound is rapidly converted superficially into the red iodide according to the equation



This distinctive reaction could be plainly observed on a sample weighing only 0.1 mg. With samples weighing 0.3 mg. or more, continued heating causes the stannic iodide to appear as a yellow to orange sublimate on the sides of the test tube above the liquid, any iodide remaining on the bottom of the tube also changing to this lighter colored form. It was further noticed that if a sample of stannic oxide is heated with the acid for a short time and then allowed to cool, a salmon-pink to red color develops in the solution above the oxide, depending upon the amount of oxide taken. This is an additional characteristic reaction for confirming the presence of stannic oxide when testing for it in this manner. Samples of the oxide weighing but 0.1 mg. were found sufficient to give this color reaction. Extraction tests with organic solvents demonstrated that this color was not due to liberated iodine. It seems likely that it results from the presence of a complex formed between dissolved stannic iodide and hydriodic acid, probably iodostannic acid. No mention of this phenomenon could be located in the literature. There is a possibility that it might be made the basis of a general analytical reaction for tin.

In general, the other insoluble oxides exhibit no characteristic reactions with concentrated hydriodic acid. When highly ignited they are all unattacked by the acid.

It has been shown (4) that the alkaline earth sulfates, though not decomposed by cold concentrated hydriodic acid, are attacked at higher temperatures, the decomposition being in accordance with the general equation



In the application of this reaction for qualitative purposes the best results are obtained at a temperature just below the boiling point of the constant-boiling acid. The use of boiling acid is not advisable, because of danger from bumping and the evolution of fumes that tend to interfere with tests for

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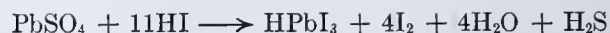
hydrogen sulfide. On the other hand, a temperature as low as 100° C. is unsuitable, since barium sulfate then reacts too slowly. By observing the best conditions it was found that definite indications of the evolution of hydrogen sulfide were given by 0.1-mg. samples of all three alkaline earth sulfates, especially when nitroprusside paper was used. Lead acetate paper is slightly less reliable under the conditions of the test, because lead iodide formed by hydrogen iodide fumes and small amounts of condensed free iodine tend to obscure any lead sulfide that may be formed. Diluted acid is not suitable for testing for the presence of these insoluble sulfates in this way.

Even very small samples of barium sulfate cannot be completely decomposed by hot concentrated hydriodic acid in a reasonable time, but a sufficient concentration of barium ion can be obtained in solution in a few minutes to respond to the usual tests. Before adding any reagent it was found best to dilute the reaction mixture to about twice its original volume and then filter. This serves in the case of barium sulfate to remove any undecomposed sample, and with large samples of strontium or calcium sulfate it removes any sulfur that may have formed from the interaction of iodine and hydrogen sulfide above the reaction mixture. The iodine remaining in solution does not seriously obscure the usual precipitation reactions for the cations if time is allowed for precipitates to settle. Definite reactions for barium by sulfuric acid precipitation and by the flame test could be obtained on a solution resulting from the treatment of a 0.1-mg. sample. Barium sulfate, unlike the other two sulfates, is apparently not attacked by 3 *N* or 1 *N* acid. In testing a solution resulting from the decomposition of strontium sulfate, addition of ethyl alcohol up to 50 per cent by volume is necessary before testing with sulfuric acid. By this technic the lower limit was found to be about 0.3 mg. The lessened sensitivity in this case apparently results not only from the greater intrinsic solubility of this sulfate as compared with that of barium, but also from the adverse effect of a high hydriodic acid concentration, since after decomposition of samples as small as 0.1 mg. with either 3 *N* or 1 *N* acid strontium ion could be detected in the resulting solution by the above method.

After decomposition of calcium sulfate samples, calcium ion was tested for in the resulting solutions after neutralization by the addition of ammonium oxalate reagent. A complication enters here when using hydriodic acid stabilized with hypophosphorous acid, since the latter apparently contains calcium as a usual impurity. Employing the pure constant-boiling acid, the solution from a 1.0-mg. sample of this sulfate gave an almost immediate precipitate of calcium oxalate. Samples smaller than this gave a precipitate only on standing for periods up to an hour, 0.3 mg. being about the lower limit for definite reaction. The lessened sensitivity of the oxalate test for calcium under these conditions evidently results from the effect of high iodide-ion concentration on the solubility of calcium oxalate, for when acid as dilute as 1 *N* was used a definite reaction for calcium could be obtained in the solution from a 0.1-mg. sample of the sulfate.

It will be noted that the difference in behavior with acid of moderate concentration can serve to differentiate barium sulfate from the other two sulfates. Hydriodic acid appears to be of greater practical value for determining whether or not a given difficultly soluble unknown contains sulfate than for obtaining a solution to be used for the usual wet tests, particularly when mixtures of alkaline earth sulfates are encountered, since then the metals present can be more readily detected by flame or spectroscopic tests.

Lead sulfate, like the alkaline earth sulfates, is decomposed by hot concentrated hydriodic acid, the reaction being in accordance with the following equation:



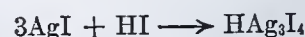
Here again a 0.1-mg. sample was found sufficient to give a distinct test for hydrogen sulfide with nitroprusside paper. Lead sulfate also dissolves in cold concentrated hydriodic acid owing to complex formation, the resulting solution having a faint yellow to deep golden yellow color, depending upon the lead concentration. The reaction in this case can be represented by the equation



On dilution of a solution obtained in this manner there precipitates out, by reason of the decomposition of the iodo-plumbous acid, characteristic golden yellow lead iodide in a very finely divided form. This behavior can be used as the basis of an identification reaction for lead sulfate. Unfortunately, the test is not very sensitive owing to the solubility of lead iodide, but samples down to 2.0 mg. gave very satisfactory reactions. For smaller samples a better procedure is to evaporate the hydriodic acid solution of the sample to dryness on the steam bath to effect the decomposition of the complex. Any characteristic crystals of lead iodide then remaining behind are easily recognized. It was found that 0.1 mg. of the sulfate was sufficient to give a definite test, regardless of whether the samples were decomposed originally with cold or with hot concentrated hydriodic acid.

The resistance of chromic dihydroheptasulfate to decomposition by hot concentrated hydriodic acid is approximately of the same order as that of barium sulfate, since complete solution of even very small samples is obtained only after long heating. No difficulty, however, was experienced in obtaining a test for hydrogen sulfide from a sample weighing but 0.1 mg. In order to obtain good tests for chromic ion in a solution prepared by treating samples of this sulfate with hydriodic acid, it was necessary to remove the excess acid by evaporation on the steam bath. The residue was then taken up in a little distilled water, and the perchromate test for chromium was performed in the usual manner on this solution. With a sample weighing 0.5 mg. the blue color in the ether layer was definite, but smaller samples gave uncertain or negative results.

The silver halides dissolve copiously in cold concentrated hydriodic acid, owing to complex formation. In the case of the iodide the reaction can be expressed by the equation



With the chloride or the bromide the reaction follows the course

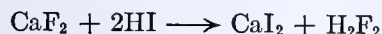


When large enough samples are used the hydrogen halide is expelled from solution with effervescence, but with very small samples evolution of the gas is not evident, since it remains dissolved in the solution. These reactions are noticeably hastened by increase in temperature and by agitation. In all three cases dilution of a solution obtained in this manner results in the precipitation of finely divided silver iodide by reason of the decomposition of the iodoargentous acid.

With the volume of acid generally used in these experiments, samples as small as 0.4 to 0.5 mg. responded to the test. In order to obtain the characteristic precipitation of silver iodide on dilution when smaller samples were taken, it was necessary either to expel most of the excess acid by evaporation or to employ initially not more than a few drops. When this was done no difficulty was experienced in obtaining a reaction from a halide sample weighing but 0.1 mg. With small samples attempts to differentiate between the chloride and bromide by collecting the evolved gas in a small volume of water and making the appropriate tests on the resulting solu-

tion were not successful, owing largely to the difficulty of preventing traces of hydriodic acid from being carried over.

It does not seem to have been previously observed that calcium fluoride is attacked by hot concentrated hydriodic acid according to the equation



This reaction, though slow even in the boiling acid, takes place rapidly enough for qualitative purposes. On small samples the decomposition appears to work about as well as when sulfuric acid is used. When the reaction was carried out in soft glass test tubes just below the boiling point of the constant-boiling acid, distinct etching of the walls of the vessels took place with samples as small as 3.0 mg. By using a more sensitive apparatus consisting of a small platinum dish covered with a piece of perforated platinum foil upon which a microscope cover glass was placed, definite etching patterns were obtained from samples weighing 0.4 mg. on heating with the usual volume of acid at 120° C. for 20 minutes. By using a smaller volume of acid, a definite test could be obtained with 0.2 mg. of calcium fluoride. Parallel experiments on a ground sample of pure fluorite gave identical results.

Though dissolved but slowly by cold concentrated hydriodic acid, anhydrous chromic chloride is rapidly dissolved by the hot acid. It was concluded as the result of experiments that the solution of the compound by this reagent follows a different course than when reducing agents like stannous chloride are used to promote its hydration. That the effect is non-catalytic with hydriodic acid is indicated by the fact that no oxidation-reduction changes are involved, and that acid of low concentration is ineffective. It appears that a definite displacement reaction is involved, which can be represented by the equation



Actual evolution of hydrogen chloride is observable when sufficiently large samples are taken. The hot solution exhibits a characteristic dark brown to nearly black color, but when cooled this changes to dark green, a rapidly reversible effect that can be repeated indefinitely. This change is apparently connected with a change in the structure of the hydrated chromic iodide in solution. With very small samples, however, the solution appears green at all temperatures. Though scarcely necessary because of the characteristic color of the compound itself and the color changes observable on dissolving it, a confirmatory test for chromium can be made on the solution in the same manner as described under the sulfate. Here again the lower limit for a positive reaction by the perchromate test was reached with a 0.5-mg. sample.

Qualitative Experiments on Mixtures

Complete investigation of the manner and extent to which the sensitivities of the foregoing tests are affected by the presence of varying quantities of one or more other difficultly soluble compounds would obviously require a vast number of experiments. However, results in certain representative cases will serve to indicate the applicability of this general method for the examination of unknown mixtures of insolubles. In these experiments the sensitivity of the test for a given compound in the presence of either 100 or 1000 mg. of some other compound was determined. In a few cases the tests were tried in the presence of two other difficultly soluble compounds.

STANNIC OXIDE IN MIXTURES. It was found possible to detect as little as 0.1 mg. of stannic oxide in the presence of 100 mg. of relatively inert compounds like silica, chromic oxide, barium sulfate, or calcium fluoride when the salmon-pink to red coloration which develops in the acid was used as

the basis of the test. In the presence of 1000 mg. of admixed compound 0.3 mg. of tin oxide could be detected. With the exception of those containing chromic oxide, red particles of stannic oxide were also observable in these mixtures. In the case of chromic oxide mixtures it was necessary, in order to obtain a reaction for the stated amounts, to filter the acid solution through a fine-grained, sintered-glass filtering crucible before making observations, so as to remove suspended fine particles which tend slightly to obscure the color reaction. The definite formation of a sublimate of stannic iodide in all the above cases occurred when the quantity of tin oxide present reached 0.5 mg.

Though they react with hydriodic acid, silver halides do not interfere with the color test. Experiments on mixtures of silver chloride and stannic oxide showed that the sensitivity is about the same as in the cases just discussed. The sublimation test is, however, slightly less sensitive with these particular mixtures, about 0.7 mg. of oxide being required to give a noticeable sublimate of the iodide.

In the presence of compounds that react with hydriodic acid to liberate iodine, direct observation of the stannic oxide reactions is not possible. Thus with calcium or strontium sulfate mixtures it was necessary to decompose the sulfate completely, decant, wash the residual particles of stannic oxide and iodide with water, and finally add fresh acid, the test then being made in the usual way. As this manipulation entails slight losses, the test under these conditions is not as sensitive. Lead sulfate behaves similarly, though it is preferable to remove the lead salt from the mixture with cold concentrated acid, followed by washing the residual stannic oxide first with acetone and then with water before performing the test. In this manner it was possible to detect 0.2 mg. of stannic oxide in admixture with 100 mg. of lead sulfate or 0.4 mg. of oxide in 1000 mg. of sulfate. Since in the presence of anhydrous chromic chloride the intense color of the solution resulting from the treatment of the sample also prevents observation of the reactions, it was necessary in this case likewise to decant and add a fresh portion of acid. The sensitivity experiments gave the same results as those on lead sulfate just cited.

Experiments on the detection of stannic oxide in the presence of two difficultly soluble compounds gave about the same results as those with single compounds and it therefore seems probable that similar small amounts of the oxide can be detected by this test in nearly any combination of insolubles likely to be met with in practice.

SULFATES IN MIXTURES. For most of these experiments strontium sulfate, taken as representative of the group of difficultly soluble sulfates, was mixed with stannic oxide, chromic oxide, silver bromide, calcium fluoride, or anhydrous chromic chloride. Since nearly identical results were obtained with the various binary mixtures, experiments with the individual pairs need not be discussed separately. With nitroprusside paper evolution of hydrogen sulfide could be detected when 0.3 mg. of the sulfate was admixed with 100 mg. each of these substances; with 1000 mg. of added insoluble, 0.5 mg. of strontium sulfate gave a positive reaction in each case. In general the experiments indicated that no difficulty should be experienced in detecting the presence of like small amounts of any of the insoluble sulfates in admixture with any combination of the other difficultly soluble compounds.

SILVER HALIDES IN MIXTURES. Silver iodide was taken as representative of the group. The presence of the silver compound was detected in each case by the reprecipitation of silver iodide on diluting the solution obtained by treatment of the solid mixture with cold concentrated hydriodic acid. Inasmuch as certain of the difficultly soluble compounds not attacked by the cold acid tend to remain in suspension, it was necessary to filter the solution before dilution. In each

case the mixture was treated with 2 ml. of acid and then filtered through a fine-grained sintered-glass filtering crucible. By adding the clear solution to about 200 ml. of water, definite reactions were obtained with samples that contained down to 1.0 mg. of silver iodide mixed with either 100 or 1000 mg. of stannic oxide, aluminum oxide, chromic oxide, barium sulfate, calcium fluoride, or anhydrous chromic chloride. Better results could be obtained if time was first taken to evaporate the filtrate to a volume of about 2 drops before diluting, 25 ml. of water being used here. In this way 0.1 mg. of the silver halide could be detected in admixture with the stated quantities of the above substances. Lead sulfate is apparently the only difficultly soluble compound that interferes with the direct detection of silver halides in mixtures by this method, since lead iodide precipitated on dilution can effectively mask a silver iodide precipitate. In such a case a convenient procedure is to filter off the mixed iodides of lead and silver, and place them in a warm concentrated ammonium acetate solution which, by dissolving the lead iodide, leaves the silver iodide in suspension so that it can be readily recognized.

General Qualitative Procedure

From the results of the foregoing experiments it is evident that the following scheme can be used for the systematic examination of an unknown insoluble or mixture of insolubles:

Add to the dry powdered sample stabilized hydriodic acid of specific gravity 1.70 in the proportion of about 5 ml. of acid for each gram of solid. After digesting with occasional stirring for about 5 minutes, filter, preferably through a sintered-glass funnel or crucible, and wash the residue with several successive 1-ml. portions of the concentrated acid. The filtrate and washings should be caught in a test tube. Transfer about half the residue to a small test tube, add 2 ml. of the acid, heat nearly to boiling, and examine for sulfates by testing for the evolution of hydrogen sulfide. Allow the solution to cool in order to observe the formation of a pink to red coloration or a yellow to orange sublimate indicative of the presence of stannic oxide. If the solution is deeply colored from dissolved iodine, decant, and add fresh acid before making the tests for tin oxide.

Use the other half of the residue for an etching test in order to detect the presence of calcium fluoride. Tests by conventional methods for the presence of silica, silicates, alumina, and other resistant substances should then be made on any residual material that fails to react with the hydriodic acid. Heat the filtrate from the above separation and test for the evolution of hydrogen sulfide in order to detect dissolved sulfate. Then transfer the solution to a small dish and evaporate nearly to dryness on a water bath in order to observe the formation of lead iodide from dissolved lead sulfate. Take up the concentrated solution or residue with about 25 ml. of water to bring about the precipitation of silver as iodide. If the presence of lead iodide interferes with the silver test, the ammonium acetate separation described in the preceding paragraph should be applied. This general system of examination should be supplemented by the more usual special tests on the original material when additional or confirmatory information is required.

Quantitative Separations

It was also found possible to make accurate separations of difficultly soluble compounds dissolved by hydriodic acid from those inert to the action of this acid. In quantitative experiments, for example, silica in the form of quartz, chromic oxide, crystallized alumina in the form of Alundum, or that prepared by ignition at 1000° C. for a number of hours, suffered no detectable loss on being heated with constant-boiling acid at temperatures between that of a water bath and the boiling point of the acid for various periods ranging from 0.5 to 7 hours. Such separations can be divided into two types, those that require the use of hot concentrated acid, and those that can be made with the unheated acid.

Of the first type are separations of alkaline earth sulfates from such inert substances. Some results obtained

on mixtures of strontium sulfate and silica are shown in Table I.

TABLE I. SEPARATIONS OF STRONTIUM SULFATE FROM SILICA

Digestion Time	SrSO ₄ Taken	SiO ₂ Taken	SiO ₂ Found	Difference Error
Min.	Gram	Gram	Gram	Gram
80	0.4119	0.1005	0.1008	+0.0003
60	0.4120	0.0518	0.0520	+0.0002
40	0.4005	0.1032	0.1042	+0.0010
40	0.2071	0.0450	0.0451	+0.0001
30	0.2055	0.0525	0.0525	±0.0000
15	0.1541	0.1147	0.1148	+0.0001
10	0.1090	0.4070	0.4072	+0.0002
10	0.0228	0.1228	0.1227	-0.0001
5	0.0225	0.0875	0.0877	+0.0002
10	0.0010	0.0959	0.0959	±0.0000

In these experiments the carefully weighed mixtures of sulfate and finely divided quartz were placed in small flasks and treated with 10 to 15 ml. of the stabilized acid, at or just below the boiling point. When decomposition of the sulfate appeared to be complete, as shown by the times given in Table I, the solutions were diluted with water and filtered through weighed glass crucibles. After washing with hot water the crucibles and their contents were dried at 110° C. and weighed.

The separation is good, and is fairly rapid unless too much strontium sulfate is present. The third result shows the danger of allowing insufficient time for the decomposition when handling larger amounts. In order to secure complete decomposition in such cases it was necessary to boil the acid, with constant stirring to prevent loss from bumping. In addition, high results may be due to the separation of some free sulfur. For these reasons the method is best applied in practice to mixtures that contain not more than about 0.2 gram of strontium sulfate.

A similar series of experiments was made using calcium sulfate. In these the time required for complete decomposition was found to be 20 minutes or less even for quantities of calcium sulfate that weighed around 0.5 gram. The method is, therefore, rapid in this case and sharp separations were obtained in all the trials. The quantitative separation of inert substances from barium sulfate by this process is possible, but is not feasible from a practical analytical viewpoint, mainly because of the long time required for the decomposition of even small samples of this sulfate.

That an accurate separation of anhydrous chromic chloride from silica can be made with hydriodic acid is indicated by Table II.

TABLE II. SEPARATIONS OF ANHYDROUS CHROMIC CHLORIDE FROM SILICA

CrCl ₃ Taken	SiO ₂ Taken	SiO ₂ Found	Difference Error
Grams	Grams	Grams	Gram
1.0318	1.0125	1.0126	+0.0001
0.6170	0.0331	0.0331	±0.0000
0.2269	0.1120	0.1119	-0.0001
0.1488	1.5854	1.5852	-0.0002

In these trials 10-ml. portions of acid were used, and only 10-minute treatments at the boiling point were required, the silica being collected and weighed in glass crucibles as before.

In Table III are shown the results of separations made by means of the cold concentrated acid.

TABLE III. SEPARATIONS OF DIFFICULTLY SOLUBLE COMPOUNDS FROM SILICA

(By treatment of mixtures with cold concentrated hydriodic acid)				
Salt	Salt Taken	SiO ₂ Taken	SiO ₂ Found	Difference Error
	Grams	Grams	Grams	Gram
PbSO ₄	0.4306	0.0656	0.0659	+0.0003
	0.3820	0.0420	0.0424	+0.0004
	0.1193	0.1080	0.1081	+0.0001
	0.1184	0.1218	0.1217	-0.0001
	0.0144	0.1150	0.1148	-0.0002
	0.0011	0.1299	0.1297	-0.0002
	0.0009	0.1027	0.1025	-0.0002
AgI	1.4292	1.0121	1.0121	±0.0000
	0.4826	0.0354	0.0357	+0.0003
	0.1157	0.0322	0.0320	-0.0002

In these experiments the carefully weighed and mixed samples were placed in glass crucibles and treated with the acid, three successive 5-ml. portions being used with the larger amounts of lead sulfate and single 10-ml. portions for the other runs. After apparently complete solution of the salt in each case, which took but a few minutes, the resulting solutions were drawn through the crucibles by suction. Since water decomposes the soluble complex compounds with the consequent precipitation of the iodides in the case of both these salts, it could not be used for the initial washing. Experiments with other solvents having shown that acetone was highly suitable, the remaining solution was washed through the crucibles with successive portions of this liquid. The final washings were then made with water, and the residual silica was dried and weighed in the usual way. Separations of this sort are not only rapid and very easy to carry out, but accurate results are obtainable.

Concentrated hydriodic acid has been found to be an excellent agent for the removal of certain precipitates, particularly silver halides, from glass or porcelain filtering crucibles without causing vessels to lose weight appreciably.

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- (1) Bodenstein, M., *Z. phys. Chem.*, **13**, 59 (1894).
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- (3) *Ibid.*, **54**, 3240 (1932).
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RECEIVED July 27, 1935. Constructed from part of a dissertation submitted by M. Gilbert Burford in partial fulfillment of the requirements for the degree of doctor of philosophy, Princeton University, 1935.

Note to Authors

IN THE preparation of manuscripts authors should address themselves to specialists in their particular fields, rather than to the general reader. If the article describes a new method, the author should endeavor to tell the complete story, so that the reader will not have to wait for succeeding contributions or duplicate the unpublished tests in order to find out whether he can apply the method in his own work.

The following is suggested as a general outline to be followed in preparing analytical methods for this edition:

1. Preliminary statement or introduction, in which the need for the method should be stated, brief reference to other methods or literature given, etc.
2. Experimental
 - Outline of proposed method
 - Description of apparatus and reagents
 - Procedure
 - Data
 - Interfering substances or conditions
 - Concentration range through which the method is applicable
 - Accuracy of the method
 - Precision of the method
3. Discussion and summary

that readers can easily duplicate the work. Loose directions should be avoided, unless the author knows that no possible harm can result from the most liberal interpretation that can be made of such expressions as "to the faintly acid solution," "wash the precipitate," "ignite," etc. If new or uncommon reagents are needed, the author should state their probable cost, where they can be purchased if rare, or how they can be prepared, if not on the market.

The author should distinguish carefully between precision and accuracy. Briefly but somewhat roughly stated, accuracy is a measure of degree of correctness; precision is a measure of reproducibility. The precision of a result does not necessarily have anything to do with its accuracy; it serves merely as a measure of the duplicability of the procedure in the hands of a given operator. No claim for accuracy should be made unless the author believes that he has satisfactorily established the correct result.

The author should be frank and define the limitations of the method. Tests dealing with the effects of foreign compounds should be made on mixtures in which the ratios of the compounds sought to the foreign compounds are varied and simulate conditions that are likely to be encountered in practice. If the author has made no such tests, he should state that he has no knowledge of the effects of foreign substances. It is desirable that possible applications of methods should be stated.

A summary or prefatory abstract should acquaint the reader with the main points of the article. This should give concisely where possible the substances determined, nature of material to which determination is applicable, interfering substances, range of concentration to which method is applicable, whether or not a sensible constant error is involved—that is, the accuracy of the method—and its precision. Either the summary or the prefatory abstract is so often used by abstractors that the author may well spend considerable time in their preparation, in order to be certain that proper emphasis is given to the main features of the contribution.

Our "Suggestions to Authors" is available to those unfamiliar with the form of manuscript and illustrations preferred by INDUSTRIAL AND ENGINEERING CHEMISTRY.



An Impact Cutting Test for Tire Tread Stocks

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THE importance of the problem of pneumatic tire tread cracking is generally recognized by rubber technologists. The closely allied problem of tread cutting, however, has received comparatively little attention in the literature (2-5, 7). This fact is surprising in view of the possible causal nature of cutting with respect to cracking. The published work on cutting of rubber stocks, referred to above, all deals with what may be termed static tests—that is, the cutting tools employed were applied to the rubber test pieces with velocities much lower than those with which a tread button impinges on an obstacle in normal service. Some of these tests (3, 4, 5) were designed for evaluating cutting resistance of rubber-insulated electric conductors. The methods described in these papers are satisfactory for evaluating the cutting resistance of rubber insulating materials, but fail in some cases to evaluate correctly the cutting resistance of tire tread stocks. In the most recent of these papers, which deals specifically with the cutting of tire treads, Clarke (1) using a slow-moving cutting tool (15 cm., 6 inches, per minute) drew conclusions concerning the relative values of various compounding ingredients in increasing or decreasing cutting resistance. None of Clarke's conclusions was radically different from those found in the impact tests described in this paper. (The unpublished preliminary work on impact cutting tests at this laboratory, carried out by J. H. Howey and B. A. Jones with a small pendulum device, led to the considerations underlying the test to be described.)

Theoretical Aspects of Tread Cutting

It should be borne in mind that the cutting resistance of a rubber stock is a very complex function of several interrelated factors, some of which are themselves complex. The most important of these factors are hardness, tear resistance, elastic modulus, tensile strength, aging resistance, and temperature. At first thought, it might seem desirable to determine the functional relationship between cutting resistance and these factors and thus evaluate cutting resistance in terms of simpler quantities. This procedure has not proved practicable in the experiments performed in this laboratory, for it was not found possible to express this relationship as a simple, single-valued function. For example, it was found that, in general, cutting resistance increased with increasing hardness but, in certain cases, a stock with a greater hardness than another stock was worse from the standpoint of cutting. Hence, it was concluded that cutting resistance should be evaluated by a special cutting test.

A distinction should be made between initiation of a cut in a tire tread and the consequent growth of the cut into a cracking or chipping failure. The initiation of the cut depends on that property which will hereafter be referred to as "cutting resistance." The growth of the cut depends greatly on tear resistance, which itself is a function of frequency of flexing, resistance to oxidation, and many other factors.

In developing an empirical test, which a cutting test must be, it is desirable to incorporate in it as accurately as possible the factors existing in service. In the case of the cutting

The problem of tire tread cutting is discussed in relation to the various measurable characteristics of rubber stocks such as tear resistance, cracking resistance, and hardness. Theoretical reasons are given for selecting a high-speed, high-load, knife-impact test for the laboratory evaluation of the cutting resistance of tread stocks. The impact cutting device used in this work is described in detail and results obtained with it are discussed in their relations to the physical variables involved, compounding trends, and road tests.

test it was possible to use the same order of impact velocities and forces with which a tread button impinges on a sharp obstacle in the road. The exact form of the cutting object could not be reproduced. Thus, it was necessary to use an arbitrarily designed wedge. A 20° steel wedge was selected mainly because it gave reproducible cuts of reasonable depths using the velocities and impact forces with which a tread button strikes an obstacle.

The impact velocity of a tread button on an obstacle of height y was calculated on the assumption that the tire is a rigid hoop of outer diameter $2a$ rolling on a horizontal plane with angular velocity ω . The expression for the impact velocity V thus deduced from the equations of a cycloid is:

$$V = \omega\sqrt{y} \sqrt{2a - y} \quad (1)$$

This expression is only approximate for a deformable pneumatic tire for, sidewise bulging neglected, only the extreme shoulder portions of the tread have pure cycloidal motion. However, Equation 1 gives at least the order of magnitude of the impact velocity in the central portion of the tread.

The impact force S was calculated as follows: Consider a body of weight P striking a relatively immovable body with velocity V and causing an instantaneous deformation d . The energy stored in the immovable body is $Sd/2$ and is equal to the sum of the kinetic energy of the moving body at impact ($PV^2/2g$) and the work, Pd , done by the movable body in traversing the distance d . Hence,

$$\frac{Sd}{2} = \frac{PV^2}{2g} + Pd \quad (2)$$

If e is the static deformation for a load P , by Hooke's law

$$\frac{S}{P} = \frac{d}{e} \quad (3)$$

Eliminating d from Equations 2 and 3 gives

$$eS^2 - 2ePS - \frac{P^2V^2}{g} = 0 \quad (4)$$

The solution of Equation 4 is

$$S = P + P \sqrt{1 + \frac{V^2}{eg}} \quad (5)$$

which relates the momentary maximum force or impact force S and the static load P . (This equation is not original with the author but is derived here for the convenience of the reader. For a similar expression see 6.)

Equation 5 can be applied directly to the case of a cutting obstacle impinging on a tire with velocity V given by Equation 1. Thus by Equations 1 and 5,

$$S = P + P \sqrt{1 + \frac{\omega^2 y}{eg} (2a - y)} \quad (6)$$

or, for small values of y ($0 < y < 2.5$ cm.) where $e \cong y$,

$$S = P + P \sqrt{1 + \frac{2a\omega^2}{g}} \quad (7)$$

In Equation 7, ω and a are known. The factor P is simply a function of y or the static load applied to a cutting edge to cause a deflection y without actually cutting the rubber.

In order to determine P for various static deflections e , a device was employed by means of which a 20° steel wedge was pressed against the contact area of the tread of a normally inflated and loaded tire. In this manner, a load-deflection curve was determined from which the values of P corresponding to various values of $e = y$ were directly obtained. Inserting these values of P into Equation 4, the impact force S was calculated. Values of impact velocity and impact force, calculated from Equations 1 and 7, respectively, are given in Table I.

TABLE I. IMPACT VELOCITY AND IMPACT FORCE
(Heavy-duty tire 81 × 15.2 cm.; rolling radius, 38.9 cm.)

Car Speed	Obstacle Height 0.25 Cm.		Obstacle Height 0.62 Cm.		Obstacle Height 2.5 Cm.	
	Velocity	Force	Velocity	Force	Velocity	Force
Km./hr.	Cm./sec.	Kg./cm.	Cm./sec.	Kg./cm.	Cm./sec.	Kg./cm.
16.1	52	62	79	163	158	775
32.2	104	124	158	326	316	1550
64.4	208	248	316	652	632	3100
96.6	312	372	474	978	948	4650

The simplest type of apparatus which could be used with these values of impact velocity and force appeared to be a steel knife falling freely under gravity. For such a device, the impact velocity would be determined by the height of free fall and the impact force by the load attached to the falling knife. The relation between the load, L , on the knife and the impact force is obtained directly from Equation 2 by replacing $\frac{V^2}{2g}$ by h and takes the form

$$S = 2L \left(1 + \frac{h}{d} \right) \tag{8}$$

where h is the height of fall and d is the depth of penetration of the knife before cutting occurs.

In the impact cutting device, described in detail below, the impact velocities ranged from 300 to 600 cm. per second, and the impact forces varied from 360 to 1200 kg. per cm. of knife edge. Comparing these actual values of velocity and force used on the apparatus with the calculated values of Table I, it is seen that the impact cutting device could be operated under conditions approximating those found in road service.

It is true that the tread rubber on a tire is mounted on a pneumatic base, whereas the test piece of the impact cutting test was a rubber block, 12.7 cm. (5 inches) in length, 1.9 cm. (0.75 inch) in width, and 3.8 cm. (1.5 inches) in height, mounted on a heavy steel platen. However, it was thought that the use of a pneumatic backing for the test block of the impact cutting device would introduce into the test a variable very difficult to control. Thus, the pneumatic backing of a tire was simulated qualitatively by using a rather tall (3.8 cm.), and therefore highly deformable, test block.

Apparatus and Analysis of Results

The impact cutting device illustrated in Figure 1 consists, mainly, of an accurate vertical slide which guides a loaded knife in approximately free fall. The slide is rigidly suspended from the top end. The knife, which is a 20° wedge of altitude 3.8 cm. (1.5 inches) and has an edge of 7.6 cm. (3 inches), impinges on a rubber test block and produces a cut which can be measured with an ordinary steel scale. The sliding Dowmetal carriage which bears the knife is constructed so as to permit different combinations of weights to be attached to it. The knife is readily detachable and is removed from the machine after each series of tests, oiled, and kept in a closed box until needed again.

The machine is also equipped with a vertically movable electromagnet with which the knife and carriage can be raised to the desired height and released by reversing the current in the coils of the magnet. The magnet is raised and lowered by means of a windlass. The slide is equipped with a number of stops (not

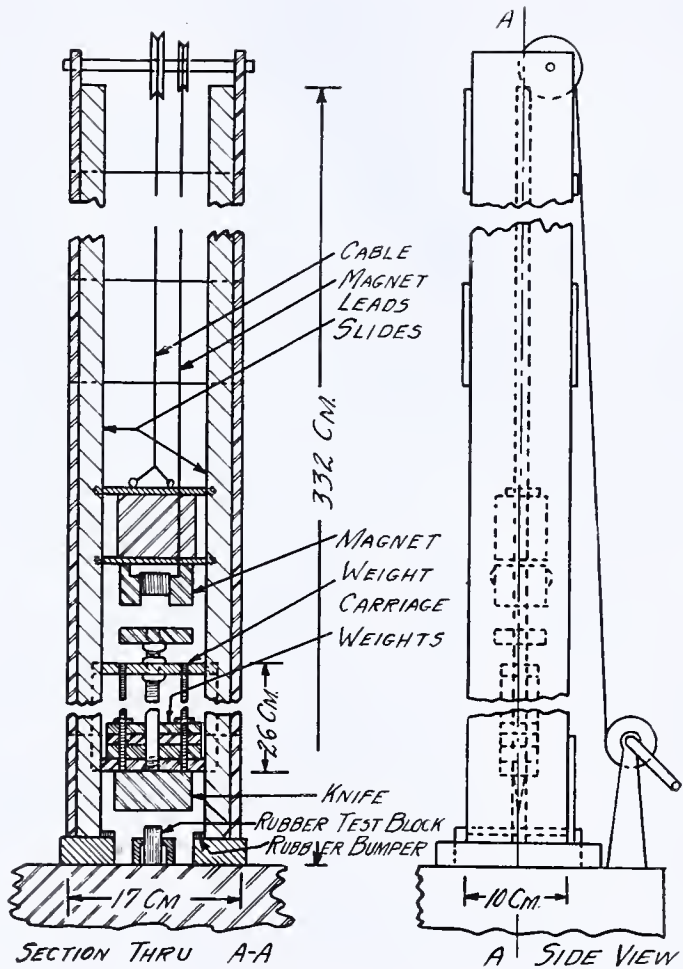


FIGURE 1. IMPACT CUTTING APPARATUS

shown in Figure 1) set at known heights, which can be used by the operator to ascertain when the carriage has been raised to the correct height. Two rubber bumpers at the bottom of the slide cushion the blow of the carriage and make it impossible for the knife edge to hit the platen face. Blocks of certain stocks deform to such an extent that the carriage hits the bumpers before completion of the cut. A trip device (not shown) mounted at the base of the slide, lights a small lamp when the carriage strikes the bumpers. In cases where the light is thus turned on, the test results are discarded.

The rubber test block, 12.7 × 1.9 × 3.8 cm. (5 × 0.75 × 1.5 inches), is placed in a holder at the bottom of the slide and rests on the large face of a steel platen 51 × 51 × 10 cm. (20 × 20 × 4 inches). The block rests on its 12.7 × 1.9 cm. (5 × 0.75 inch) face with its long axis perpendicular to the knife edge. Two cuts are made in each block at positions 3.2 cm. (1.25 inches) from the ends of the block. The deeper cuts are usually uniform in depth across the width of the block and can thus be measured with a steel scale after slitting through the rubber remaining at the bottom of the cut. The shallow cuts are, in general, less regular in depth than the deep cuts. However, with a little practice, the operator can estimate the average depth of the shallow cuts without much difficulty.

The cutting knife is of hardened steel and is carefully ground in the form of a 20° wedge. The feather edge is removed from the knife with a fine abrasive cloth. The sharpness of the knife changed with use but, by always running a control stock simultaneously with an experimental stock, it was found that the relative cutting results were essentially uniform over a period of 2 years. In this study of the aging of the knife edge, the effect of the aging of the rubber was avoided by using new samples.

In the method of testing adopted as standard, at least six test blocks of each stock or cure to be tested are cured in a 12-cavity mold in a press, the temperature of which is very carefully controlled. The blocks are then set aside for 1 week to allow the cutting resistance to come to a stable state. The hardness is then measured with a Firestone 1.36-kg. (3-pound) penetrometer (8) at various points on the 12.7 × 1.9 cm. face of the blocks. Two cuts are then made in each block with the impact cutting machine, as described above. Thus, using six blocks, it is possible to obtain twelve cuts in each stock or cure. These cuts are usually made at 2 or more loads chosen to give a depth of cut vs. load (D vs. L) curve. The cutting velocity is usually

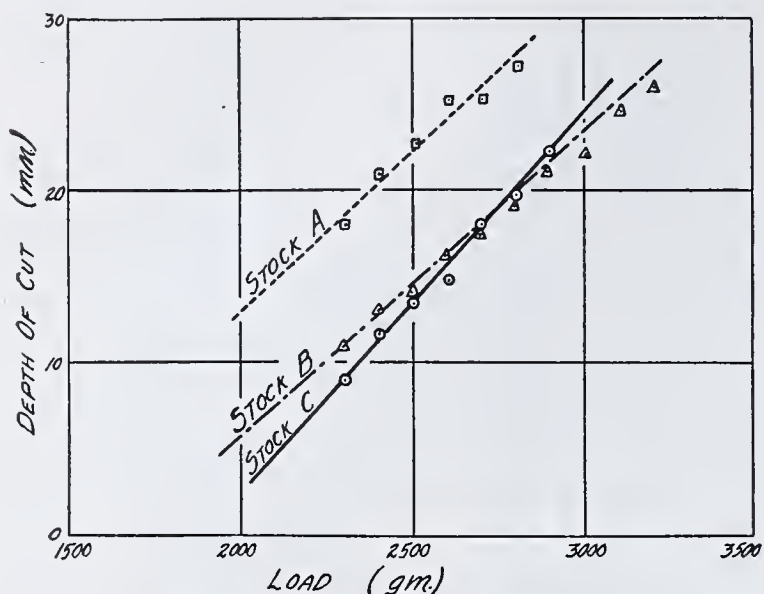


FIGURE 2. DEPTH OF CUT vs. IMPACT LOAD
20° knife, velocity 488 cm. per second

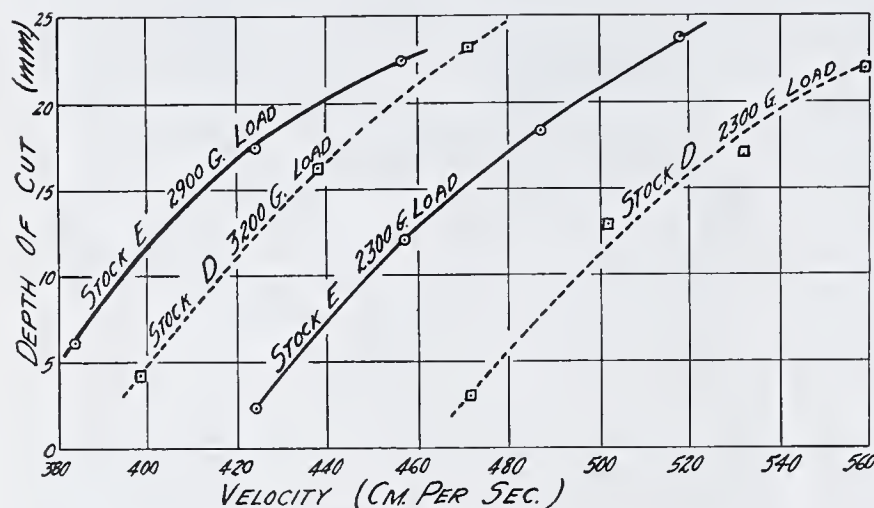


FIGURE 3. DEPTH OF CUT vs. IMPACT VELOCITY
20° knife

set at 424 cm. per second (13.9 feet per second). In practically every case the D vs. L curve is linear (Figure 2).

To be very exact, there are two physically independent indexes of cutting resistance—i. e., the slope of the D vs. L curve and the extrapolated load intercept. However, it is difficult to interpret data on the basis of two indexes. Hence, the load necessary to give a 25-mm. cut, L_{25} , has been selected as a single cutting index. This index, L_{25} , has been found very satisfactory, in that results arrived at through its use agree with road test results and with results evaluated by means of the slopes and load intercepts of the D vs. L curves.

Functional Relationships

As mentioned above, the relationship between depth of cut and load is linear. That both the slope and load intercept vary for different stocks is clearly demonstrated in Figure 2. The relationship between depth of cut and velocity at constant load is not linear, however (Figure 3). In general, the D vs. V curves are convex upward, though occasionally a curve which is concave upward is found. Unlike the D vs. L curves, the D vs. V curves do not cross in the range of velocities investigated. The practice of running tests at a single velocity is therefore justified.

The curves of Figure 4 show that L_{25} , a measure of the cutting resistance, decreases rapidly with increasing temperature. In making these tests, the test blocks were kept in an ice box

TABLE II. CUTTING RESISTANCE vs. RESISTANCE TO TEAR

Stock	L_{25} Grams	Hand Tear Estimate
A	4300	Best
B	4040	Very good
C	4180	Very good
D	4230	Very good
E	4350	Good
F	4390	Fair
G	4360	Fair

or oven until the center of the blocks had reached the desired temperature, as measured by a mercury-in-glass thermometer inserted in a hole in the block. The tests were then run immediately to minimize temperature changes occurring after removal from the oven or ice box. This dependence on temperature indicates the necessity of recording the room temperature for all tests.

The index of cutting resistance, L_{25} , generally increases with hardness [Firestone 1.36-kg. (3-pound) penetrometer] as is shown in Figure 5. However, in several cases, distinct reversals occurred—for example, stock IX vs. stock X and stock VII vs. stock VIII.

Cutting resistance does not always correlate with tear resistance. This fact is clearly shown in Table II, where two stocks which appear to be best from the cutting standpoint show up as distinctly inferior to the others from the tear standpoint.

The accuracy of the results of the impact cutting test depends upon the number of tests averaged. For example, where six blocks of a given stock were tested, the mean deviation was 4 per cent; where twelve blocks were tested, the mean deviation was 3 per cent. In individual cases the accuracy is much greater and can be determined in each case—for example, the mean deviations for the tests of Table IV were much less than 3 per cent.

Compounding Trends in Resistance to Cutting

The cutting resistance generally increased with the carbon black loading, as is shown in Figure 6. To obtain these data, the carbon black content in a commercial mercapto-benzothiazole tread stock was varied so as to give loadings varying from 38 to 76 parts by weight per 100 parts of rubber. It may be seen that the cutting resistance increased with increasing carbon black loading up to a loading of 67 per cent and then began to decrease. The existence of this maximum in cutting resistance with respect to carbon black loading has very little practical significance, since 67 per cent black is considerably above present practical compounding limits for

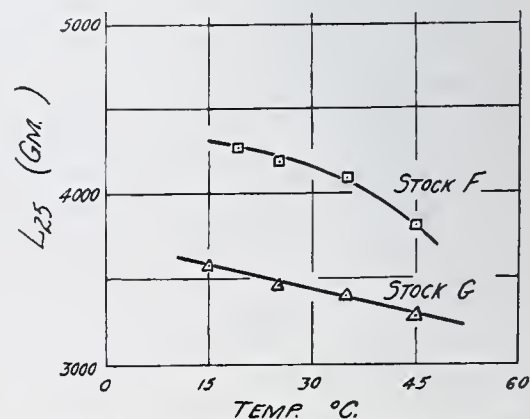


FIGURE 4. CUTTING RESISTANCE vs. TEMPERATURE

20° knife, velocity 424 cm. per second

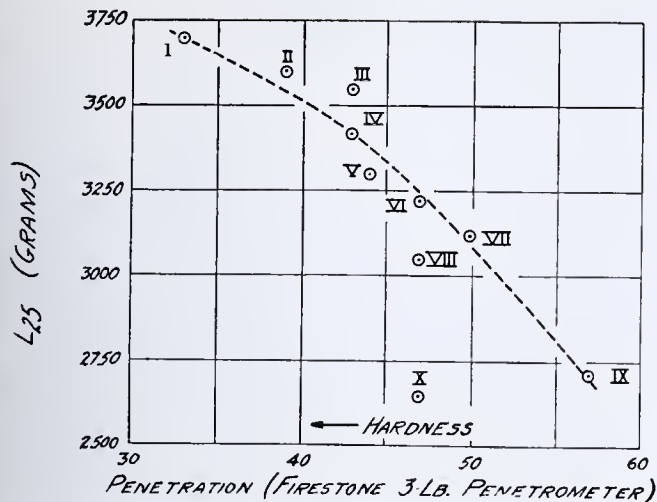


FIGURE 5. CUTTING RESISTANCE vs. HARDNESS
Ten stocks; each point average of 12 tests; 20° knife; velocity 424 cm. per second

treads. However, the fact that the cutting resistance increases to that point indicates that, for special types of service where cutting resistance is the major consideration, the loading of carbon black should be increased above the limits considered satisfactory for other types of service.

The effect upon the cutting resistance of varying the amount of carbon black in a mercaptobenzothiazole tread stock where glue is used is shown in Table III. The addition of 5 per cent glue had no appreciable effect on the cutting resistance; furthermore, the cutting resistance increased with increasing black loading to a maximum at approximately 57 parts by weight per 100 parts of rubber.

TABLE III. CUTTING RESISTANCE AS A FUNCTION OF CARBON BLACK LOADING WITH GLUE USED AS A SOFTENER

Per cent by Weight on Rubber Glue	Carbon black	L ₂₅
0	49.4	4600
5	49.4	4650
5	53.7	4760
5	57.0	5000
5	60.0	4990

Comparison of Impact Cutting with Road Tests

Great care must be exercised in comparing the results of a laboratory cutting test with road test results, for most so-called cutting tests on the road involve cracking as well as

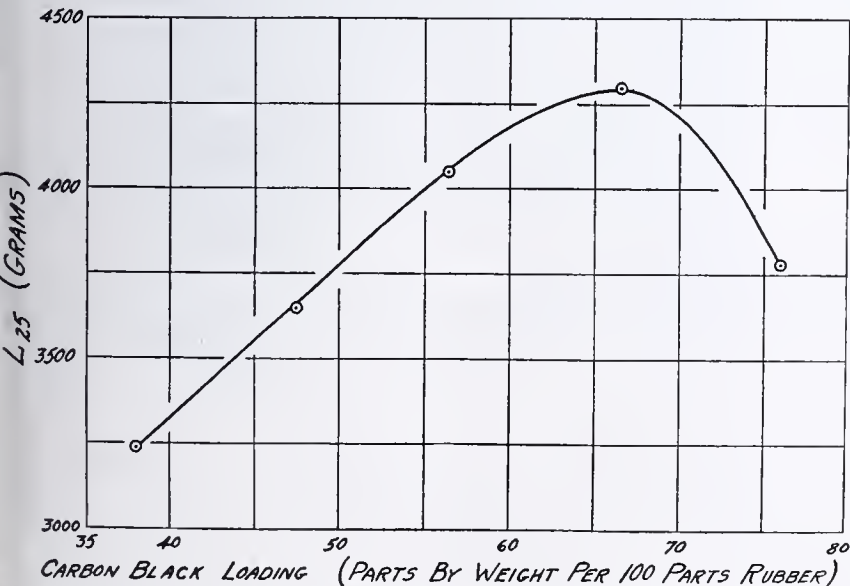


FIGURE 6. CUTTING RESISTANCE vs. CARBON BLACK LOADING
20° knife, velocity 424 cm. per second

cutting. In fact, it was found necessary to devise a special road cutting test. In this test, half-and-half tires mounted on a truck were run at low speeds over a specially constructed road upon which were strewn sharp pieces of furnace slag, broken insulators, etc. The tires were removed from the rims, after 200 to 500 miles of this service, in a badly cut and chipped condition. The treads were then cut up in such a manner that the areas of all the individual cuts could be measured. The amount of cutting sustained by a stock in the test was assumed to be proportional to the total area of the cuts. Six stock comparisons were made in this manner. Cutting test blocks were cured from sections of the extruded treads which were actually used in the test tires and impact tests were made in the standard manner.

The results are given in Table IV. The results of the impact cutting test correlated with the road test results in all cases.

TABLE IV. IMPACT TESTS vs. ROAD TESTS

Tire	Stock	Road Test Evaluation	(81 × 15.2 cm. tires)
			L ₂₅ Grams
I	A	Slightly better	3270
	B		3270
II	C	Better	3700
	D		3270
III	E	Better	3240
	F		3150
IV	G	Worse	3180
	H		3270
V	I	Better	3600
	J		3260
VI	K	Worse	3310
	L		3590

Conclusion

The impact cutting device described in this paper is recommended for testing the cutting resistance of tread stocks because of its simplicity and the accuracy with which its results agree with road test results. The fact that the device was designed on semi-quantitative theoretical grounds gives some additional confidence in its results. It is possible that other cutting devices, designed with no regard to theory whatsoever, might operate as well as the impact device. However, it is felt that, since most laboratory tests on rubber stocks are necessarily largely empirical, it is well to attempt to design a testing machine which will operate in the ranges of the variables found in service.

Acknowledgment

The author desires to acknowledge the work of B. A. Jones, who designed the impact cutting device and performed the preliminary tests, and to thank N. Johnston and R. J. Bonstein for their helpful suggestions, and N. A. Shepard under whose direction the work was done.

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A Differential Refractometer

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THIS refractometer was designed to be a rapid and reliable instrument for determining concentrations of solutions too dilute to permit the use of the Pulfrich or immersion refractometers. It makes use of the bending of a ray of light when passed through a rectangular cell containing a triangular compartment, the former being filled with pure solvent and the latter with solution. This part of the instrument is similar in principle to the Ketteler (2) and Haber-Löwe (1) refractometers, but is much more practical because of the new method of observing and measuring the deflection and of determining the zero reading.

The complete instrument is shown in Figure 1. The upper diagram in Figure 2 shows the essential parts of the refractometer, while the lower diagram shows the path of the light ray.

The achromatic lens, L , projects through the cell an enlarged image of the slit, S_2 , at point F , 110 cm. from the lens. This image is broken up into three bright interference bands by the double slits, S_3 , which are 0.31 cm. (0.125 inch) wide and 0.31 cm. (0.125 inch) apart. The appearance of the interference bands and cross hairs is shown in the circle. These interference bands are observed by the microscope, M , having cross hairs in the eye piece. Readings are taken by means of the position of a small-angle water prism, P , in a glass cell which slides on a 60-cm. steel metric scale. This prism is moved along the scale until the interference bands are brought back to the zero position. It does not displace the interference bands at all when at the focal point of the microscope, but when moved toward the cell it displaces the image nearly in proportion to the distance moved from the zero point, F . The mounting for this prism has guides that slide along the sides of the steel scale and prevent it from rotating more than 0.02° . Larger rotations would affect the readings. It is made as thin as possible. The collimator of a spectroscope serves very well for the lens, L , and slit, S_2 , if the edges of the slit are ground smooth on an oil stone. The lens has a focal length of 20 cm. The light source, J , is a 100-watt opal-glass electric light bulb. The larger slit, S_1 , protects the end of the collimator tube from the heat of the lamp. The collimator tube supporting S_2 is surrounded by a larger tube to protect it from drafts which would make the readings erratic. A Gaertner M101 microscope is suitable to observe the interference bands. All parts of the refractometer are mounted on a piece of 10-cm. (4-inch) channel iron 125 cm. long.



FIGURE 1. COMPLETE INSTRUMENT

The triangular cell, shown in the upper part of Figure 3, is built on the under side of a piece of plate glass, having a 2-cm. round hole in the middle. The optical faces are pieces of ordinary commercial plate glass and extend 1 cm. below the bottom of the triangular cell, which is 1.2 cm. deep and has an inside length of 8.5 cm. The angle between the faces is 137° . One piece of heavy platinum foil is used for the bottom and back of the cell because of its higher heat conductivity. A narrow slot 1.5 mm. deep is cut in the plate glass so that the platinum foil is mortised into the glass. This prevents the cement from covering much of the optical surface and gives it much greater strength. This cell requires 5 cc. of liquid in order to transmit bright interference

bands. The outside cell, shown in the lower part of Figure 3, is made by cutting a half cylinder from a bottle 8 cm. in diameter and 9.5 cm. long and cementing a piece of plate glass on each end. The only precautions necessary in making the cells is that the ends of the outside cell be parallel within 0.1° and the line of intersection of the two optical faces of the triangular cell be perpendicular within 0.3° to the surface of the channel iron.

The plate-glass top which supports the triangular cell is held against the projecting end of the rectangular cell by a spring at the other end, preventing rotation as well as movement toward or away from the light source. The small prism, P , containing water is made by cementing two pieces of thin plate glass (1.5×3 cm.) together with a separator at one end. The angle between the faces is $2^\circ 55'$. The axis of this prism must be parallel to that of the cell prism within 0.3° . A shutter placed at O can be turned up or down to cut out the light from either the upper or lower parts of the triangular cell. Both light paths are left open except when the solution is so very dilute that the two sets of bands overlap. With pure water in both compartments, the readings through the upper and lower compartments should be identical. If these readings are different, it is due to a strain in the triangular cell.

The first step in adjusting the instrument is to fill the rectangular cell with distilled water, leaving the triangular cell out for preliminary adjustments.

Open slit S_2 wide and move it toward or away from the lens until an image of it is projected at point F on a piece of white paper. Close the slit slowly, observing the image of the slit through the microscope. When the slit can just barely be seen, refocus the microscope on this image. Interference bands should then appear. The quality of the bands can be improved by slight changes in the width of the slit and position of the microscope. When sharp interference bands are obtained, replace the triangular cell and fill it with water. Look at the slit from point O . If the light coming from both double slits does not appear the same, move the triangular cell until it lets both beams of light pass through it equally well and make a final readjustment of the microscope to give the best interference bands.

Table I shows readings taken every minute for 14 minutes, after filling the triangular cell with a solution of 0.05 N sodium chloride. The last reading was taken after leaving the solution in the cell until the next day. The readings became constant in 5 minutes after filling the cell. The reading at 10 minutes is an accidental error of observation due to eye fatigue, from looking continuously at the interference bands. Eliminating this value and the first four taken while the temperature was being equalized, the average deviation from the mean is 0.042 mm. or an average error of 0.032 per cent for this 0.05 N solution of sodium chloride. For a 0.1 N solution the average error would be one-half as great, or 0.016 per cent. However, the error does not decrease below this value at higher concentrations because the bands become colored through dispersion of the salt.

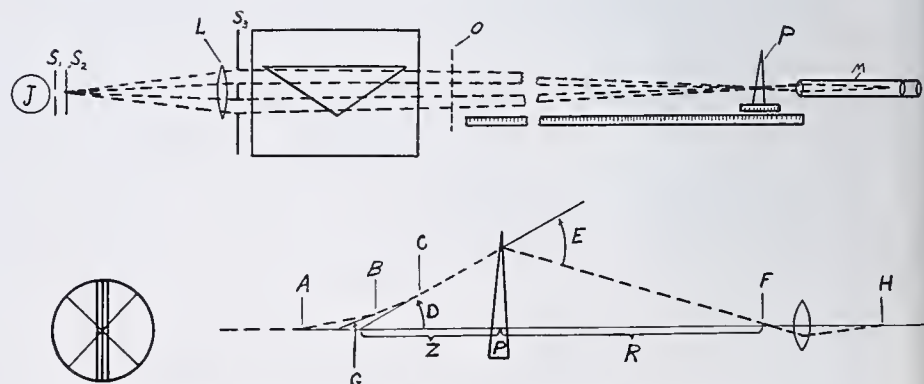


FIGURE 2. REFRACTOMETER AND PATH OF LIGHT RAY

The zero reading changes considerably, owing to warping of the instrument by temperature changes and relieving of strains, but the difference between the zero reading and the solution reading remains constant. Therefore it is always necessary to take a zero reading immediately before the solution reading. It is important to keep the instrument out of drafts when in use or the zero reading will change so rapidly that the reading will be erratic. If the cell is opened for only a few seconds, sufficient evaporation occurs to cool the liquid so that one must wait several minutes after covering again for the temperature to equalize.

Table II shows the effect of changing the position of the triangular cell in the rectangular compartment. The only small displacement that would affect the reading is moving the triangular cell toward the light source. Since the glass plate is pressed against one end of the rectangular cell, it can always be replaced so that the reading will be affected less than 0.03 mm., a negligible error.

TABLE I. READINGS

Time Min.	Zero Reading	Solution Reading	Difference Cm.
1	0.08	13.30	13.22
2	0.04	13.28	13.24
3	0.04	13.28	13.24
4	0.06	13.29	13.23
5	0.07	13.28	13.21
6	0.07	13.28	13.21
7	0.09	13.30	13.21
8	0.12	13.33	13.21
9	0.10	13.32	13.22
10	0.10	13.36	13.26 ^a
11	0.11	13.32	13.21
12	0.12	13.33	13.21
13	0.13	13.35	13.22
14	0.14	13.35	13.21
Next day	0.25	13.47	13.22

^a Accidental error.

TABLE II. EFFECT OF CHANGING POSITION OF CELL

Prism Position	Zero Reading	Solution Reading	Difference
Normal position	1.77	14.98	13.21
0.5° to right	2.27	15.48	13.21
0.5° to left	0.86	14.07	13.21
2 mm. to side	1.67	14.88	13.21
6 mm. toward light	1.76	15.16	13.40
Original position	1.51	14.72	13.21

The sensitivity of the instrument increases rapidly as the angle of the triangular cell is increased, but angles larger than 137° are not recommended since the bands become weaker and more diffuse as the angle is increased. The water prism, *P*, gives the instrument more than twice the range that it would have with a prism of ordinary glass. The higher dispersion of the water compensates considerably for the dispersion due to the solution in the refractometer. A scale reading of 60 cm. corresponds to a difference in refractive index of about 0.002 or a deviation of about 0.5° by the cell. For such small angles, the displacement of the movable prism is practically proportional to the difference in refractive index. The scale readings for certain differences in refractive indices were calculated, using eight-place trigonometrical functions, for the mean of the two beams which give the interference bands. The difference in refractive index, with water as the reference liquid, is given within one part in ten thousand by the formula

$$\Delta n = (33355 S - 2.83 S^2) \times 10^{-9}$$

where *S* is the scale reading in centimeters. The second term amounts to only 0.1 per cent for a 13-cm. scale reading and for smaller readings it may be neglected. For the maximum scale reading of 60 cm., the second term amounts to 0.5 per cent. Since the difference in refractive index in general is not exactly proportional to the concentration, it is more

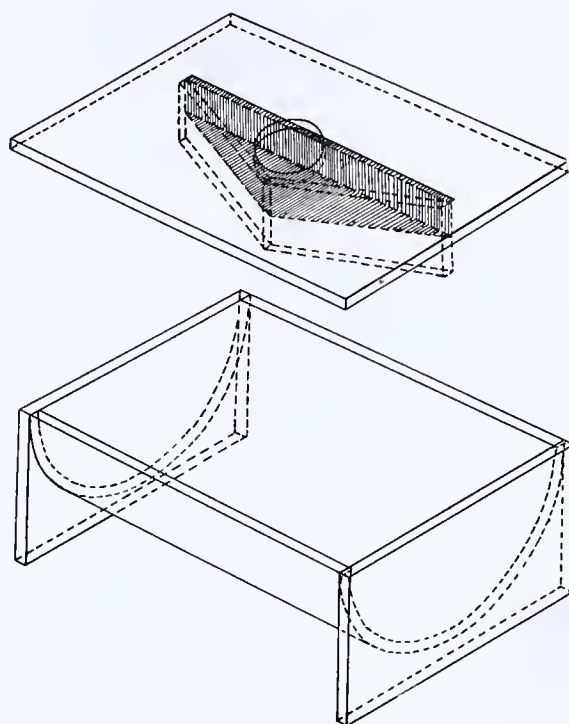


FIGURE 3. DIAGRAM OF CELLS

convenient for analytical purposes to calibrate the instrument directly in terms of concentration of the solution to be analyzed. If the solution has a refractive index below that of the reference liquid, the prism, *P*, is reversed on the scale. If absolute differences of refractive indices are desired, it is easier to calibrate the instrument with two solutions of known refractivity than to measure the angles of the prisms. This refractometer has been used for transference number determinations. For the small concentration changes involved, the concentration was proportional to the scale reading, within 0.1 per cent. Using this 137° cell, $\Delta n = 0.002003$ for a 60-cm. or maximum scale reading. This would be the reading given by a 0.23 *N* sodium chloride solution. If more concentrated solutions are to be analyzed, they may be diluted or a prism with a smaller angle may be used.

Summary

A differential refractometer has been developed that uses white light and has a sensitivity of 5×10^{-7} . It has been used to determine the concentrations of aqueous solutions with refractive indices from 0.0004 to 0.002 greater than pure water with an accuracy of 0.1 per cent. This corresponds approximately to 0.04 to 0.2 *N* sodium chloride solutions. The scale readings are nearly a linear function of the difference in refractive indices. Readings can be taken much more easily and rapidly than with the liquid interference refractometer.

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RECEIVED May 29, 1935.

CORRECTION. In the paper on "A Modified Persulfate-Arsenite Method for Manganese" by E. B. Sandell, I. M. Kolthoff, and J. J. Lingane [*IND. ENG. CHEM., Anal. Ed.*, 7, 256 (1935)] the 15th line from the bottom in the first column of page 258 should read "Dissolve 1.2 to 1.3 grams of pure arsenic trioxide—," instead of "Dissolve 2.5 grams of pure arsenic trioxide—."

I. M. KOLTHOFF

An Electrically Heated Melting Point Apparatus

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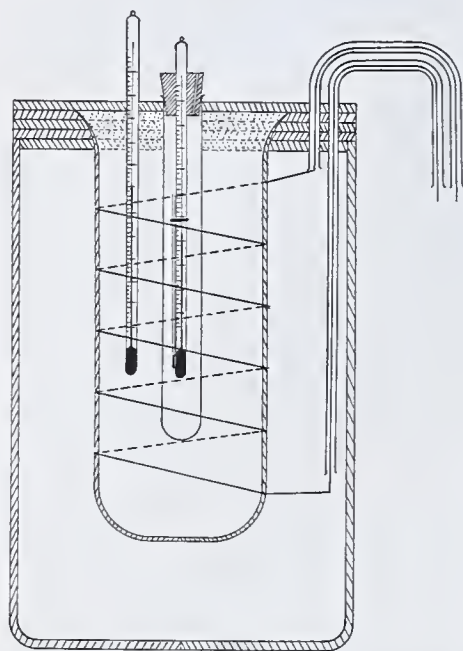


FIGURE 1. MELTING POINT APPARATUS

ing points up to about 310° C., with a reproducibility of within 0.5° C.

Apparatus

A round battery jar (Figure 1), about 150 × 230 mm., is fitted with a cover composed of four disks of asbestos board, each 5 mm. thick and 150 mm. in diameter, cemented together by means of water glass. The diameter of the bottom disk is reduced so that it fits snugly into the jar. Two small holes, about 25 mm. apart, are drilled 12 mm. from the outer circumference of the cover to take two Pyrex tubes 3 mm. in inside diameter. In addition to these holes, a tapering hole is cut in the center of the cover to hold an 80 × 180 mm. Pyrex tube, closed at one end, firmly centered in the jar. This tube has two 3-mm. holes, 12 mm. apart, drilled 25 mm. from the top, and two similar holes just at the start of the curve at the bottom.

The tube is set into the hole in the cover and then wound with five equally spaced turns of Nichrome ribbon 0.15 × 0.0125 cm. (0.06 × 0.005 inch), the ribbon being anchored by means of the small holes at the ends of the tube and then brought up through the glass tubes in the cover to serve as lead-in wires. The individual turns of ribbon about the tube are securely fastened in place by spotting each turn with a drop of paste made of short asbestos fiber and water glass. The holes in the 80 × 180 mm. tube and the ends of the lead-in tubes are also sealed with this paste.

A fifth disk of asbestos board, similar to those already described, is drilled to take the two small lead-in tubes, a hole to support a Pyrex test tube, 18 × 150 mm. (to hold the melting

point thermometer and capillary), centered in the 80 × 180 mm. tube, and a fourth hole to insert a 0° to 250° C. thermometer midway between the tubes. This board is put in place, the lead-in tubes are inserted, and it is then "tacked" down to the main portion of the cover in several spots with water glass.

Number 14 gage rubber-covered wire is used throughout the electrical circuit, connection being made to the Nichrome ribbon by means of brass wire connectors. The electrical input to the heating coil is controlled by means of a 5-ampere Allen Bradley radiostat and measured by an ammeter having a range of 0 to 5 amperes in 0.2 ampere divisions. For safety and convenience, a toggle switch and a 10-ampere fuse are inserted in the circuit.

In order to make the apparatus a complete unit, capable of being moved about the laboratory quickly and easily, a base 40 × 27.8 × 18.75 cm. (16.375 × 11.125 × 7.5 inches) was constructed with 1.25-cm. (0.5-inch) angle iron. This base served to support not only the jar but all the other electrical equipment as well. As neither the size nor shape of this base affects the operation of the apparatus, it may be varied to suit the individual's requirements. However, a very definite idea of its construction may be obtained from Figure 2.



FIGURE 2. PHOTOGRAPH OF MELTING POINT APPARATUS

Operation

The manipulation of the apparatus should not entail any difficulty after a few

trial runs are made to familiarize the operator with its behavior.

The capillary, containing the sample, is attached to an Anschütz thermometer of appropriate range and set into the inner test tube, the thermometer being held in place by means of a cork stopper with a very small slit up the side to allow for air expansion within the tube. The current is then turned on and the input regulated so as to attain a rapid increase in temperature until a point approximately 25° below the supposed melting point of the substance is indicated on the auxiliary thermometer.

The input is then reduced until a steady rise of about 3° per minute is attained in the inner tube. As the melting point

TABLE I. TEMPERATURE FOR GIVEN INPUT

Elapsed Time	1—Ampere Input		2—Ampere Input		3—Ampere Input		4—Ampere Input		5—Ampere Input	
	Temp.	Temp. rise	Temp.	Temp. rise	Temp.	Temp. rise	Temp.	Temp. rise	Temp.	Temp. rise
Min.	° C.	° C./min.	° C.	° C./min.	° C.	° C./min.	° C.	° C./min.	° C.	° C./min.
0	26.0	..	26.0	..	24.5	..	28.5	..	26.5	..
5	41.5	3.4	63.0	6.9	87.0	12.1
10	48.0	..	79.0	7.5	131.5	13.7	202.5	23.1
15	62.4	2.88	108.0	5.8	173.0	8.3	244.0	8.3
20	72.8	2.08	127.0	3.8	191.6	3.7	262.5	3.7
25	79.4	1.32	139.1	2.4	203.0	2.3	271.0	1.7
30	41.0	..	84.2	0.96	146.5	1.5	211.0	1.6	280.2	1.8
35	42.4	0.28	87.6	0.68	151.5	1.0	217.2	1.24	284.4	0.84
40	43.6	0.24	90.5	0.58	155.0	0.7	221.5	0.86	285.6	0.24
45	44.8	0.24	92.6	0.42	157.0	0.4	224.2	0.54	287.6	0.40
50	45.2	0.08	94.5	0.38	157.2	0.04	224.5	0.06	288.6	0.20
55	45.7	0.10	95.5	0.20	157.4	0.04	289.7	0.22
60	45.8	0.02	96.2	0.14
65	46.0	0.04
70	46.2	0.04

is approached the input is further gradually reduced until, at a point about 3° below the supposed melting point of the substance, a temperature rise not exceeding 0.75° per minute is obtained.

Table I, listing temperature for a given input at various elapsed times, should be considered as being only approximate. The given temperatures are those indicated on an Anschütz thermometer placed in the inner test tube. No account was taken of the lag of the apparatus at any particular point. During the preliminary rapid rise of temperature, up to about 200° C., this lag is a noticeable and variable factor, depending mainly upon the rate of temperature rise and must be taken into account for accurate temperature control. A close approximation of its magnitude may be obtained by placing a long-range thermometer midway between the tubes, as is illustrated in Figure 1.

As indicated in Table I, temperatures up to about 284° C., with the correct rate of temperature rise at that point, may be obtained by using 5 amperes. However, the time required to reach this point may be considerably shortened and the useful range of the apparatus increased to approximately 310° C., at the expense of a slight overload, by using 5.33 amperes.

Experimental

It having been stated (1) that melting point apparatus employing an air bath yields results that are consistently higher than those obtained in a liquid bath, it was deemed advisable to check the authors' apparatus against one employing a bath of phosphoric acid, previously heated as directed by Snell (2) to determine the magnitude of this variation under present conditions. The bath, having a volume of 1.5 liters, was electrically heated and mechanically stirred during each determination. The rate of temperature rise, in all cases, was between 0.5° and 0.75° C. per minute

at the melting point. The temperature at which the substance became a clear fluid throughout was defined as the melting point. The U. S. P. X defines this as the "end of melting."

The melting points as determined in the authors' apparatus (first figure) and by the modified Snell method (second figure) were as follows: salol 42.6° and 42.4°, acetanilide 115.0° and 114.5°, phenobarbital 176.0° and 176.0°, saccharin 225.0° and 224.5°, phenolphthalein 261.0° and 260.8°. The results indicate that the melting points obtained in the air bath are slightly higher than these obtained in the liquid bath. However, as the apparent melting point of a substance is a somewhat variable figure, depending not only upon the diameter and thickness of the capillary tube used and upon the slight variations in filling the tube but also upon the operator, a second series was obtained by means of the authors' apparatus to determine how closely triplicate determinations would check. All figures were obtained by one operator on successive days.

The minimum and maximum values of the observed melting points were found to be as follows: salol 42.5° and 42.6°, antipyrine 110.5° and 111.0°, phenobarbital (The phenobarbital used in this series was drawn from a lot other than that from which the material used in the previous determination was taken.) 174.8° and 175.1°, caffeine 235.0° and 235.4°, phenolphthalein 260.7° and 261.0°. The maximum difference obtained was 0.5°. If this figure is taken as the maximum experimental error, the differences in results obtained with the described apparatus and the phosphoric bath are insignificant.

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RECEIVED October 19, 1935.

Prevention of Foaming in Crude-Fiber Determinations

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THE mechanics of crude-fiber determinations is made tedious by a tendency of many materials to foam during digestion. The custom of breaking the foam by blowing through an auxiliary tube or through the condenser requires the constant attention of the analyst.

The author has found that a fine jet of air projected on the center of the boiling liquid is as effective in dispersing the foam

as a larger current of air. Furthermore, if proper precautions are taken, a fine jet of air may be projected on the surface of the digesting material throughout the digestion period without increasing evaporation. The diagram illustrates a convenient arrangement of apparatus for routine crude-fiber determinations, in which compressed air is let into the digestion flasks by means of capillary tubes through the condensers.

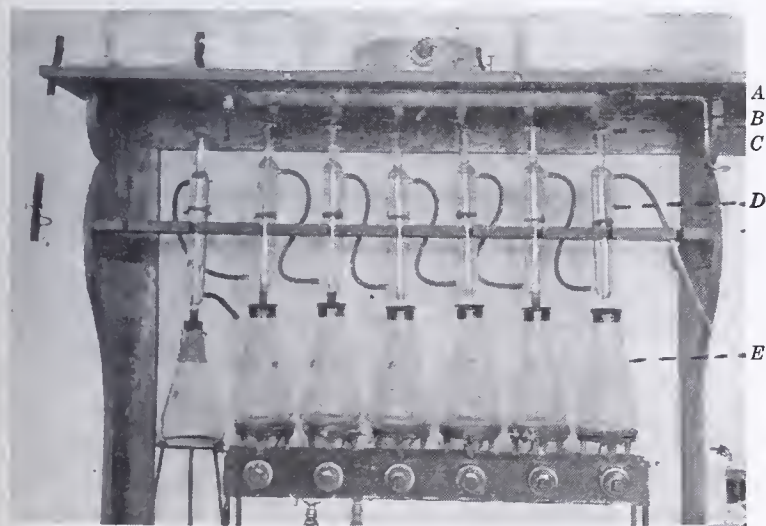
Tube A is a compressed air supply from a laboratory pump to the apparatus connected with a capillary tube, C, through stopcock B. Tube C may be of any suitable diameter, but is drawn out at the tip to a diameter of about 1 mm. To prevent possible breakage, tube C is made just long enough to reach the bottom of condenser D. A stream of air is thus projected onto the surface of the digest in flask E.

The author has used this apparatus for more than a hundred determinations consisting of mixed feeds and packing-house residues. Analyses were made by the official method (1). There was a great saving of time on the part of the analyst, and good results were obtained.

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RECEIVED October 28, 1935.



An Automatic Recording Balance

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An automatic, electrically operated, continuous recording balance fitted with oil damping and counterbalanced for an initial load of 100 grams is described. Losses in weight up to 17 grams, with an accuracy in the order of 0.01 gram, are recorded without manual attention by means of an automatic device which places weights, in the form of steel bearing balls, upon the pan. Recording is performed, through the use of a timed spark, upon a paper chart carried on the drum of a variable-speed kymograph which has a range of from 12 hours to 6 days.

STUDIES of the rate and magnitude of the moisture losses occurring during the drying of macaroni products involve a series of determinations at relatively frequent intervals extending over a period of several days. In this type of work it is necessary either to remove samples for the determination of residual moisture or to weigh directly a sample suspended within the drying cabinet. The removal of material at frequent intervals disturbs the drying schedule, introduces sampling errors, and is subject to the possibility of changes in moisture content during the operations involved. In view of these difficulties, direct weighing of a sample suspended from a balance external to the cabinet is preferable. Since the actual drying is carried out in a stream of conditioned air, as described by Binnington and Geddes (2), a certain amount of motion is imparted to the sample which renders it essential to use a type of balance insensitive to this condition. In order to overcome the inconvenience of frequent weighings at regular intervals over extended periods and to secure a continuous record of the weight loss, the automatic recording balance described in this paper was developed.

The literature on recording balances is rather meager. The simplest form appears to consist of a mirror attached to the beam of a standard balance, registering by means of a light beam upon sensitized paper; such devices have been described by Abderhalden (1), Tryhorn and Wyatt (7), and Köhler (5). The weight range covered by this type of balance is rather limited and the recording system somewhat cumbersome. A method based on the automatic addition of uniform increments of weight has been described by Oden (6). This was later improved by the addition of an electromagnetic balancing system and a suitable recording device. The perfected instrument is described by Coutts et al. (3) and is known as the Oden-Keen automatic recording balance. The balance proper is essentially a standard analytical model which is not suited to weighing material subject to a certain amount of motion. It accordingly became necessary to design a balance based on somewhat different principles from those hitherto described.

The instrument was built up around an old type of unequal-arm balance (ratio approximately 5 to 1) and is designed

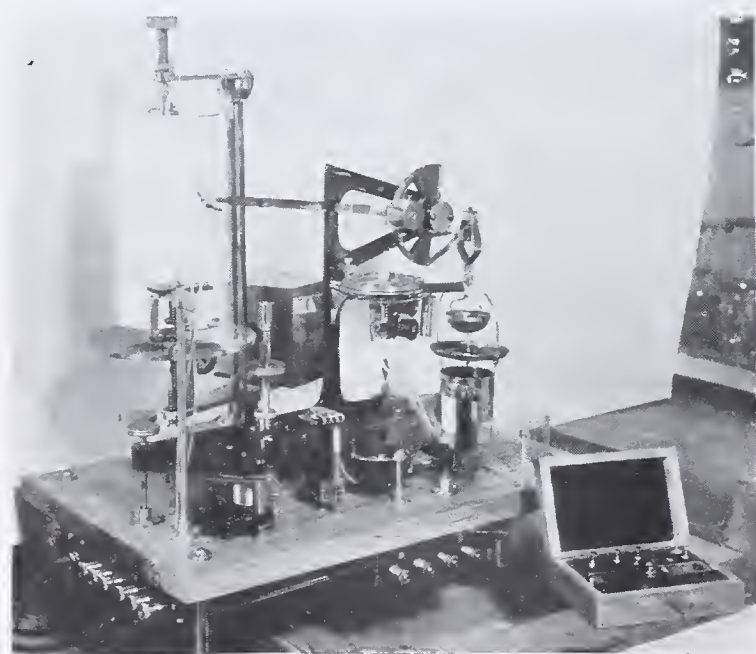


FIGURE 1. PHOTOGRAPH OF AUTOMATIC RECORDING BALANCE

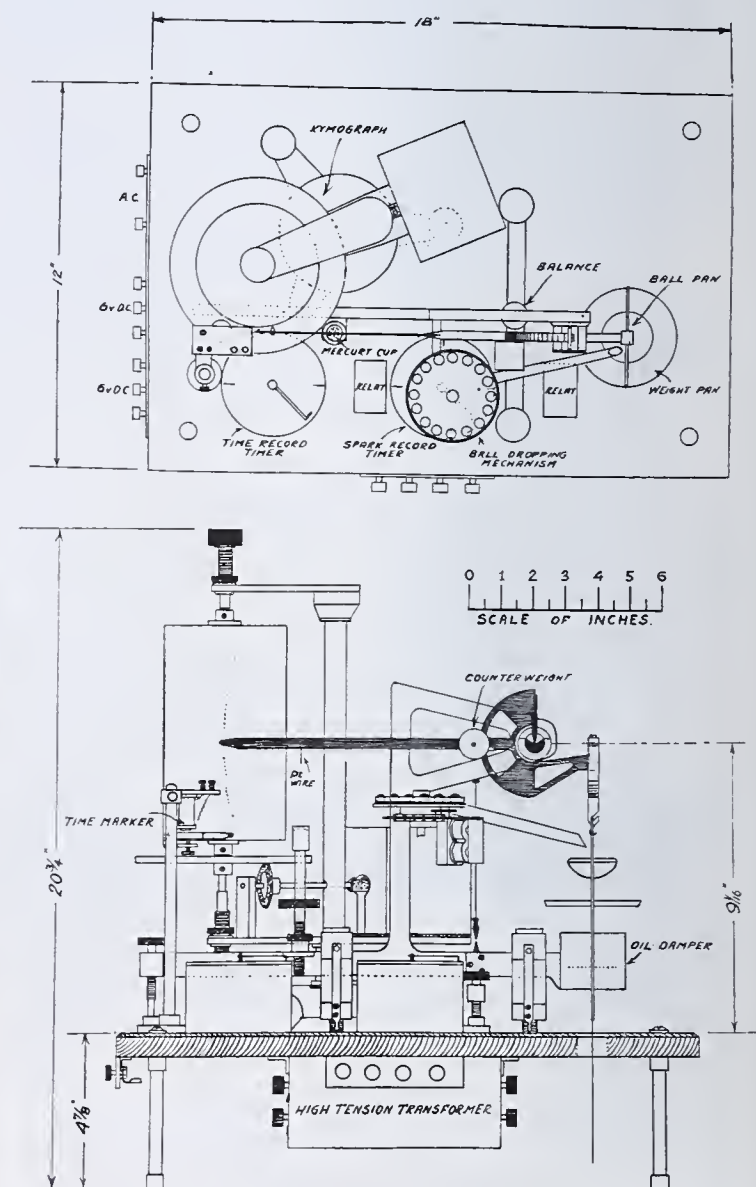


FIGURE 2. DETAILS OF COMPLETE ASSEMBLY

Above, plan

Below, elevation

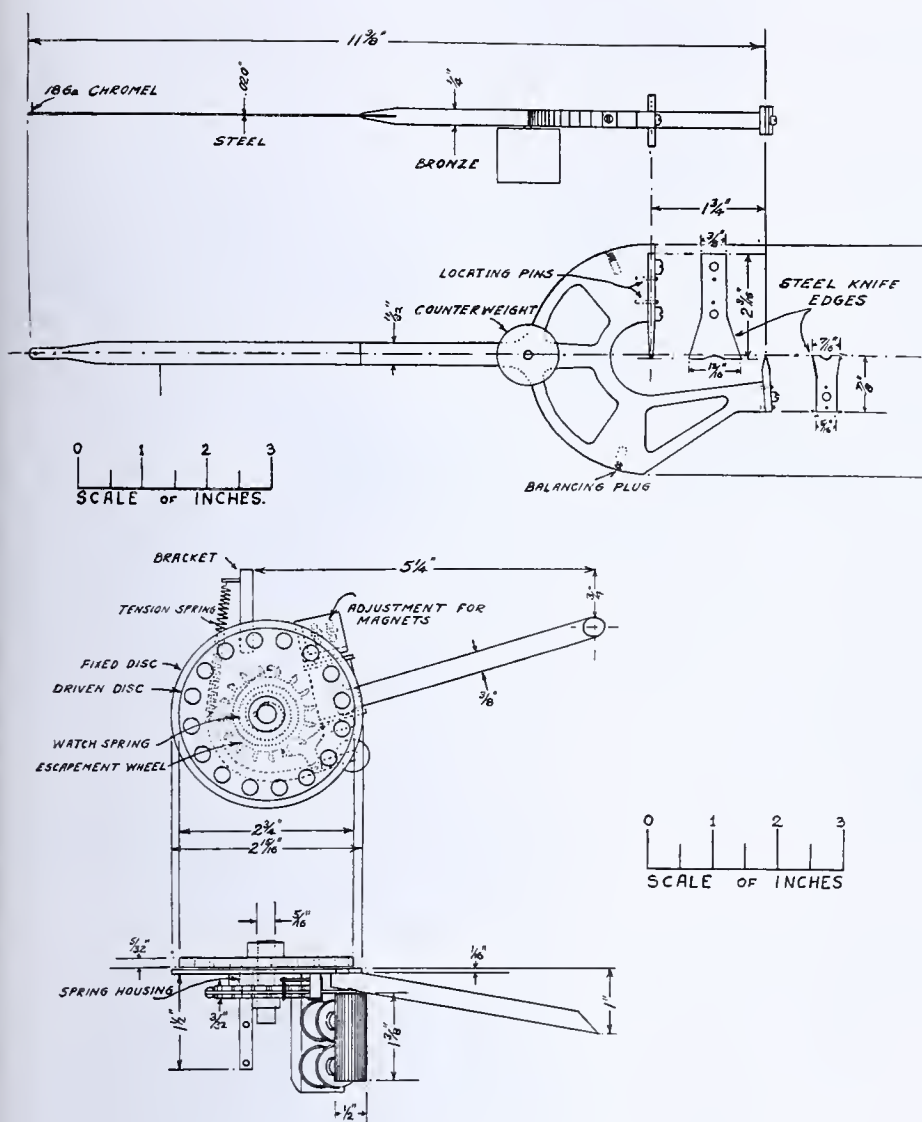


FIGURE 3. DETAILS OF BALANCE BEAM (ABOVE) AND BALL-DROPPING MECHANISM (BELOW)

primarily for recording loss of weight, although it may be used without alteration for weight increases of not more than 1.5 grams. The entire assembly is illustrated in Figures 1 and 2.

The balance is adjusted to carry a 100-gram load, and its oscillation is reduced to a minimum by a simple oil damping device. The actual record is produced on a paper chart carried upon the drum of a variable-speed kymograph by means of a high-tension spark. This spark is produced between a nichrome point on the end of the balance beam and the metal of the recorder drum, thus burning a small hole through the chart; the duration is about 0.2 second and the frequency

interval may be varied from 15 to 60 seconds. A time record is also produced upon the chart by a suitable device. When the beam reaches the lower end of its travel, which corresponds to a weight loss of 1.04 grams, a platinum wire contacts with mercury and actuates a device which places a 1.04-gram steel bearing ball upon the balance pan, thus restoring the beam to its starting position. The record thus obtained consists of a series of descending curves, from which the total loss in weight, the hourly loss, and the rate of loss over any time interval, may be calculated. The entire assembly is mounted as a unit upon a heavy oak base standing on tall brass pillars. In use, it is placed on top of the drying cabinet, the sample being hung over a stirrup attached to the balance pan by means of a fine nichrome wire which passes through a small hole drilled in the top of the cabinet.

Balance

The balance is of very simple design, the remodeled beam details being shown in Figure 3.

It was remodeled from an old type "ash" balance (sold by A. Gallenkamp & Co., Ltd., London, England, 4) designed to carry a load of 30 grams and indicating weight directly to 0.01 gram. The scale and part of the frame were removed, a counterweight was fitted, and the position of the smaller knife edge altered to obtain stable equilibrium. The spring-type pan arrest was also removed and a simple oil damper fitted. The pan suspension was extended to enable the attachment of a sample carrier which was suspended within the cabinet. A small additional pan for receiving the ball weights was also installed and a nichrome wire point, 0.46 cm. (0.19 inch) long, 18 gage, attached to the end of the beam. All these alterations and additions were made prior to counterbalancing for a 100-gram load. The balance was fixed upon the base by means of brass cups into which the leveling screws fitted; these cups were screwed onto the base after final location of the instrument.

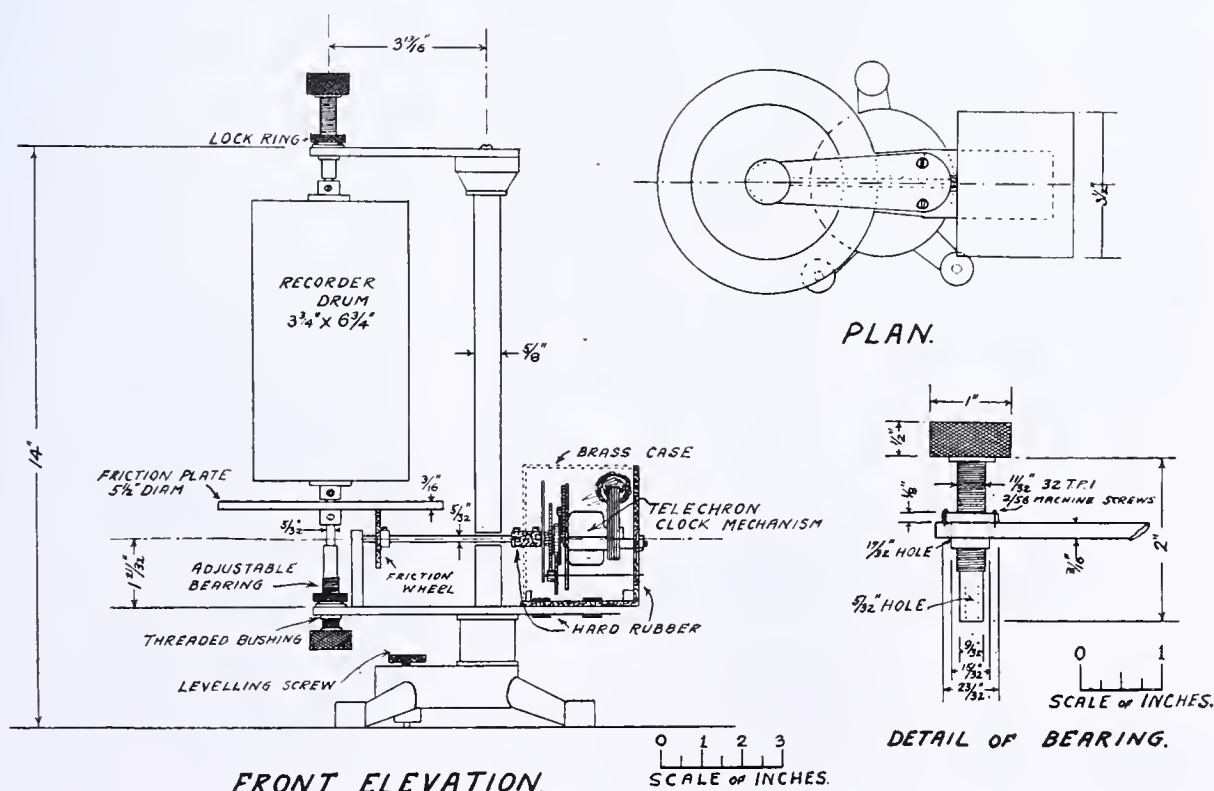


FIGURE 4. DETAILS OF KYMOGRAPH

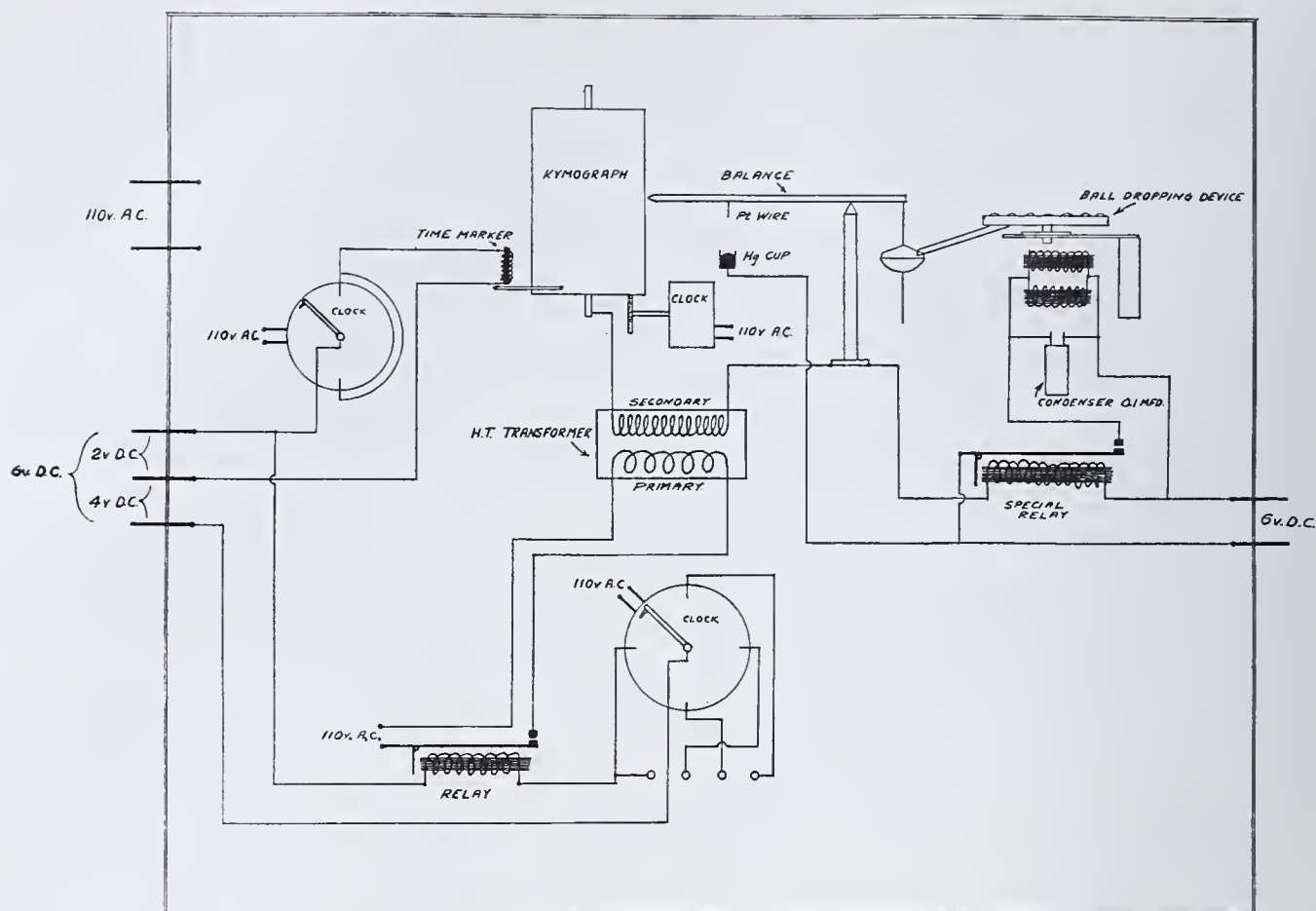


FIGURE 5. WIRING DIAGRAM

Kymograph

The kymograph is illustrated in Figure 4 and consists of a brass drum 93.75×16.875 cm. (3.75×6.75 inches) mounted in vertically adjustable bearings and driven through the medium of a friction wheel and plate from the hour spindle of an electric clock. It is essential to employ a clock mechanism of the self-starting (telechron) type and it must be completely insulated from the metallic support of the kymograph. It is also necessary to solder the loose-friction gear to its spindle to prevent slippage. The purpose of fitting vertically adjustable bearings is to allow for regulation of the friction drive and also to accommodate various sizes of friction wheels. This simple device permits the use of a very wide range of chart speeds. A time record is produced upon the lower edge of the chart by means of an electromagnetically operated pen (Figure 1) which traces a continuous line. At 0.5-hour intervals this pen is moved a short distance at right angles to the base line by a small electromagnet, the operation of which is controlled by suitably spaced contacts on the face of an electric clock fitted with a brush contact on the minute hand. Like the main drive clock, this should be of the self-starting type and the loose friction gear must be firmly attached to its spindle. Fixing this gear makes it impossible to adjust the position of the hands by the regular time-set knob, but prevents any possibility of slippage due to the abnormal load imposed on the mechanism. The two contacts are of thin (0.25-cm., 0.01-inch) sheet brass set on edge in slots made in a hard-rubber face.

Spark Timer

The spark is produced by means of a small transformer designed for operating gaseous tubes (Jefferson No. 721-171, 2500 volts, 25-ma. capacity), the secondary terminals being connected to the kymograph and balance supports, respec-

tively. Timing of the spark is effected by an electric clock fitted with four evenly spaced contacts 0.05 cm. (0.02 inch) wide, and a brush contact on the second hand. The leads from the four contacts are carried to terminals placed at the front of the base and arranged so that connecting the first two gives a spark every 30 seconds, connecting all a spark every 15 seconds, and with no connections, a spark every 60 seconds. In order to minimize oxidation of the clock contacts, the alternating current supply to the transformer is controlled by means of a standard telephone relay fitted with heavy tungsten contacts. The current flowing through this relay is in the order of 15 to 20 milliamperes. The clock employed is treated exactly like those driving the kymograph and record timer.

Weight-Handling Mechanism

The weights employed consist of selected standard steel bearing balls, 0.32 cm. (0.25 inch) in diameter, weighing approximately 1.04 grams each, a maximum variation of 3 mg. being allowed.

The actual device employed to place these weights upon the balance pan is based upon that described by Coutts et al. (3) in which the balls are placed in holes located around the periphery of a thick brass disk rotated electromagnetically by means of a ratchet and pawl. Considerable difficulty was experienced with this form of drive and it was finally abandoned in favor of the arrangement illustrated in Figure 3. The disk carrying the balls is driven by means of a few turns of watch spring, the rotation being controlled by a mechanism similar to that of a clock escapement. It is operated by an electromagnet on 6 volts direct current and drawing about 7 amperes. This current supply is controlled by a special type of delayed-action relay (Siemens Bros. of Canada, No. A-108) which functions when the beam reaches the lower end of its travel by means of a platinum wire attached to the

beam contacting with mercury in a steel cup. This cup is adjusted vertically by means of a fine thread screw. The position of the beam at the moment of contact is taken as a base line for establishing the weight scale.

The special type of delayed-action relay is fitted with a nickel sleeve surrounding the core. After the operating circuit is broken, the armature of this relay stays closed for a period of approximately 100 milliseconds, thus eliminating the possibility of a number of impulses being given to the ball-dropping mechanism by "jittering" at the platinum-mercury contact. This jittering gave considerable difficulty and was overcome only by use of the above-mentioned relay.

Wiring

The wiring diagram is illustrated in Figure 5. Two separate 6-volt batteries are employed. This is necessary in order to avoid interaction of the high- and low-voltage circuits and to maintain a satisfactory spark at the gap between the kymograph drum and the point on the beam. This distance should be from 1 to 3 mm., and after being satisfactorily located, the kymograph should be permanently fastened to the base.

Operation

As designed, the balance will record a loss of 17 grams in weight without attention. Should the loss exceed this amount, it is necessary to rewind the disk and insert more balls.

To place the balance in operation, a 100-gram weight is attached to the suspension wire, and the mercury cup adjusted until the platinum wire just fails to make contact. A mark is then made upon the chart at this point, and weights are added in 0.1 gram increments, the chart being marked at each point up to 1 gram. An additional 0.04 gram is then added to establish the upper limit of the scale. The weights are then removed and replaced by a ball. The 100-gram weight is then replaced by the sample, exactly 100 grams being secured by balancing to the upper point on the weight scale. If exact adjustment in this way is not feasible, approximately 100 grams may be taken, the exact amount being ascertained by the addition of balance weights to the pan, which remain during the duration of the test. Upon completion of the record, the chart is removed, weight lines are drawn on at 0.1-gram intervals, and time lines inserted with a guide cut to the curvature of the arc traveled by the recording points. Total or intermediate weight values may then be read directly from the chart.

The apparatus has been employed in drying and equilibrium studies for some time with highly successful results, it being possible to read the record to 0.01 gram, equivalent to 0.01 per cent, using a 100-gram sample.

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Semi-Micro-Cottrell Boiling Point Apparatus

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VARIOUS types of boiling point apparatus constructed according to the Cottrell principle (1) have been designed by previous workers—Davis (2), Swietoslawski (5, 6), those at the Petroleum Refining Laboratory of the Pennsylvania State College (4), and others—for the accurate determination of boiling points on a macro scale. Although the Cottrell principle of bubbling the liquid and vapor in equilibrium over the thermocouple or thermometer seems logical and practical, it is believed that no method has been developed on this principle for the accurate determination of the boiling point of a small volume of liquid. The construction of a microapparatus not only suitable for the determination of boiling points accurate to 0.1° C., but also adaptable to differential use, presents an interesting problem, and is the object of this research. The apparatus of Davis and of Swietoslawski (2, 5, 6) were said to be very accurate, but because of the greater probability of accurate results and greater ease of manufacture with reduction in size, the design of the Petroleum Refining Laboratory of the Pennsylvania State College was used, decreased to about one-tenth the size. A scale drawing of the apparatus is shown in Figure 1.

The glass tube, A, contains the hot junctions of the thermocouples, cemented in place at J. B is provided to determine the boiling point spread, and also, in the present case, for convenience in determining the minimum quantity of liquid upon which a boiling point can be determined. Heat is applied to the apparatus by winding it between G and H with 0.9 meter (3 feet) of enameled thermocouple wire of 14.3 ohms per meter (4.35 ohms per foot) resistance. This wire is connected to the alternating current line through a rheostat which is used to vary the heat input.

The inner part of the apparatus is a separate unit made of two pieces of Pyrex tubing, C and D, of 5 and 10 mm. outer diameter, respectively, held together as shown by a very short tube, I, which forms a canal between them. Several file marks are made on the bottom end of D to permit free circulation, since this unit rests on the outer unit at a level indicated by the point F. The tube of smallest diameter, C, is then free, not touching the outer unit at all. Thus, the liquid placed in the apparatus is heated by the external heating unit between G and H and boils up through the space between C and D, to be bubbled out on the thermocouple junction.

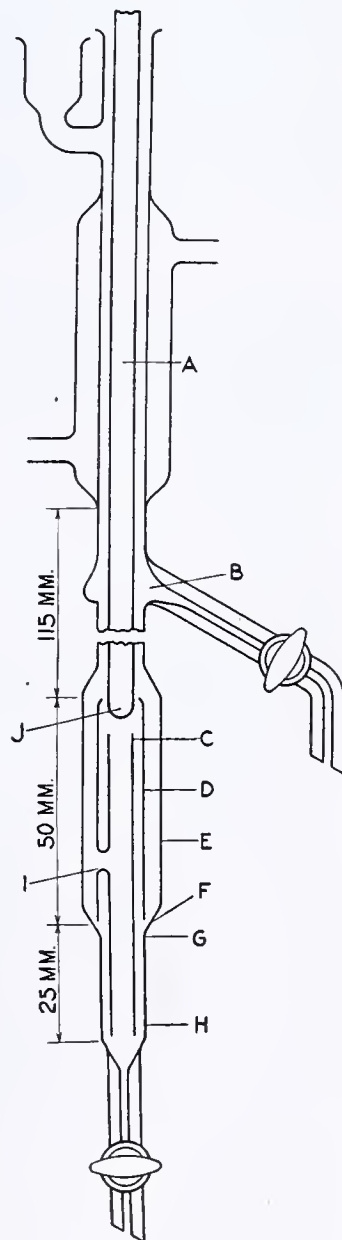


FIGURE 1



TABLE I. BOILING POINT DATA

(Charge, 5 cc. of carbon tetrachloride; barometer, 727.1 mm.; n_D^{20} , 1.4600.)

Time	Left Cc.	Millivolts per Couple	Boiling Point Found ° C.	Calculated Vapor Pressure Mm.
Thermocouple position as shown in Figure 1				
3:49	5.0	3.426	75.07	727.3
3:51	5.0	3.426	75.07	727.3
3:54	4.5	3.426	75.07	727.3
3:58	4.0	3.426	75.07	727.3
4:10	3.5	3.426	75.07	727.3
4:13	3.0	3.426	75.07	727.3
4:16	2.5	3.426	75.07	727.3
4:19	2.5	3.426	75.07	727.3
4:21	2.3	3.426	75.07	727.3
4:22	2.0	3.426	75.07	727.3
4:28	1.5	3.427	75.09	...
4:30	1.2	3.424	74.96	...
Thermocouple 1 cm. above position indicated in Figure 1				
4:40	5.0	3.426	75.07	727.3
4:48	4.5	3.426	75.07	727.3
4:52	4.0	3.426	75.07	727.3

TABLE II. BOILING POINT DATA

(Charge, 6 cc. of distilled water; barometer, 730.7 mm.; thermocouple position as shown in Figure 1.)

Time	Left Cc.	Millivolts per Couple	Boiling Point Found ° C.	Calculated Vapor Pressure Mm.
10:10	6.0	4.619	98.90	730.5
10:15	6.0	4.619	98.90	730.5
10:20	6.0	4.619	98.90	730.5
10:25	5.5	4.619	98.90	730.5
10:30	5.0	4.619	98.90	730.5
10:35	4.5	4.619	98.90	730.5
10:40	4.0	4.619	98.90	730.5
10:45	3.5	4.619	98.90	730.5
10:50	3.0	4.619	98.90	730.5
10:55	2.5	4.619	98.90	730.5
11:00	2.0	4.619	98.90	730.5
11:06	1.5	4.621	98.94	...
11:10	1.0	4.620	98.92	...

TABLE III. BOILING POINT DATA

(Charge, 5 cc.)

Liquid	n_D^{20}	Boiling Point Expt. ° C.	Calcd. ° C.	Barometer Mm.
Carbon tetrachloride (redistilled)	1.4600	75.07	75.06	727.1
Benzene (redistilled) thiophene-free	1.4997	78.53	78.55	725.6
<i>n</i> -Heptane. ^a California Chemical Co.	1.3878	97.20	97.24	731.4
Isooctane ^a 2,4,4-trimethyl pentane, Röhm and Haas	1.3918	97.74	97.75	727.8
Water (triple distilled)	98.90	98.90	730.5
Toluene (to be used for nitration), Barrett Co.	1.4933	109.02	109.04	727.8
Chlorobenzene (redistilled)	1.5238	130.07	130.04	728.6

^a Approved by the Bureau of Standards for knock-rating purposes.

tions at *J*. The liquid and condensed vapor are then allowed to return downward through *C*, whence they may again follow the same path. The outermost tube, *E*, of 17 mm. outside diameter served as an auxiliary jacket.

For thermal measurements multiple-junction copper-copel thermocouples of gage No. 28 enameled wire were used. The copel wire was from Hoskins, and the copper wire from John R. Roebing's Sons Co. There were ten hot and ten cold junctions, each of which was soft-soldered together and then insulated by covering with Durite resin, using acetone as a solvent. Each series of junctions was enclosed in a glass tube. The junctions were held in place at the very tip of the tube by a small amount of litharge and glycerol cement. If the cement extends to any appreciable distance beyond the junctions, an appreciable heat loss may be introduced. A Leeds and Northrup double-range potentiometer indicator, portable precision type, No. 8662, was used, which had recently been checked at the factory.

The cold junction was an ice bath constructed according to the technic of Aston of this laboratory. Finely shaven distilled water ice in a 1-liter Dewar was used, and 50 cc. of distilled water were added to insure intimate contact. Thermocouples from the same spools of wire had been found to conform to the curve drawn by substituting in the Bureau of Standards equation for this same spool of copel wire. Two points on the curve were checked—the transition point of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and the boiling point of water. The transition point of $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is 32.384°C . (3). The equation is as follows:

$$E = 42.074 T - 0.04986 T^2 - 0.0000310 T^3$$

E is expressed in microvolts and *T* in degrees Centigrade.

Experimentation

The data given in Tables I to III were obtained using the apparatus illustrated. A determination of the boiling point range of a liquid can be made in 15 minutes or less.

Discussion

From these and other data of a similar nature it was found that the mean deviation of experimental from calculated boiling point was 0.02°C . The calculations were made from existing vapor pressure-temperature data. As may be seen by reference to Table III, all were accurate to 0.1°C . It was also found that the use of a jacket around the apparatus was expedient; that, starting with 5 cc., a 60 per cent take-off could be made without causing any variations in the millivolt readings—i. e., boiling point measurements accurate to 0.1° can be made on as little as 2 cc. of liquid—that the method of wiring by winding with thermocouple wire between *G* and *H* (Figure 1) was most satisfactory; that the variation of heat input by as much as 100 per cent did not affect the millivolt readings; and that bumping was negligible.

A 2-cc. apparatus of the same sort was designed and constructed. The boiling points obtained with it were consistently lower than those obtained with the 5-cc. apparatus under the same conditions. For this reason the take-off was removed from the smaller apparatus and replaced by a side return for the condensed vapors. Results obtained with this apparatus were also low in spite of the use of a jacket. A possible explanation of the lowness of the results lies in the fact that with decrease in size the ratio of surface exposed to volume of liquid increases. This would introduce a greater heat loss and well might be the cause of the low results.

Experiments have been conducted on a 1-cc. apparatus of similar design, but the same difficulties are encountered as with the 2-cc. apparatus. None of the various adaptations in structure have completely removed the sources of error. The readings are consistently lower than calculated. The specific causes for this are not known, but are being investigated.

Summary

With an apparatus of 5-cc. capacity boiling points were found which were accurate to 0.1°C . The mean deviation for the liquids tried was 0.02°C .

Starting with 5 cc. of pure material, a take-off of 60 per cent may be made without causing any variation in the millivolt reading obtained.

Work has been done on a smaller apparatus of the same Cottrell type, but the results were not satisfactory.

Acknowledgment

Acknowledgment is due to Frank C. Whitmore and to Dorothy Quiggle for their valuable suggestions throughout the course of this research.

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ANALYTICAL EDITION

INDUSTRIAL AND ENGINEERING CHEMISTRY

HARRISON E. HOWE, EDITOR

Surface-Tension Measurements of Viscous Liquids

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By allowing a small air jet to impinge on the surface of a liquid, there is produced a small depression whose depth is an inverse function of the surface tension of the liquid. This procedure is particularly suited to viscous liquids.

THE usual methods for surface-tension measurements fail when applied to highly viscous fluids. The following method, developed by one of the authors (A. H. P.) in 1932 and tested by the other (E. W. G.) in 1934 is based upon the observation that if a small air jet be allowed to impinge on the surface of a liquid, an indentation or depression of the type shown in Figure 1 is produced. The depth of this depression has been found to be an inverse function of the surface tension. The method is at its best when applied to liquids which are nonvolatile, viscous, and transparent.

The general arrangement of the apparatus is shown in Figure 2, where *A* is a glass tube drawn down to a bore of about 0.8 mm. at its lower end which is separated by about 3 mm. from the liquid surface, *C*. While there is nothing critical about the dimensions of the cell, *B*, the thickness of the fluid layer in the direction *LM* was chosen as 10 mm. The depth of the depression is 1 to 2 mm. since instability sets in when the depth is made considerably greater. Measurements of the depth of the depression are carried out with a short-focus Gaertner telescope, *M*, supplied with a micrometer eyepiece reading to 0.01 mm. Illumination is effected by means of the small lamp, *L*, which is replaced by an arc lamp when the liquids are nearly black. Light coming over the top of the liquid is cut out by the opaque shield, *S*. Since it is necessary that the distance between the end of the glass tube, *A*, and the liquid surface be kept constant—a condition difficult to realize by attempting to fill the cell always to the same level—an arrangement of the type shown in Figure 3 was adopted.

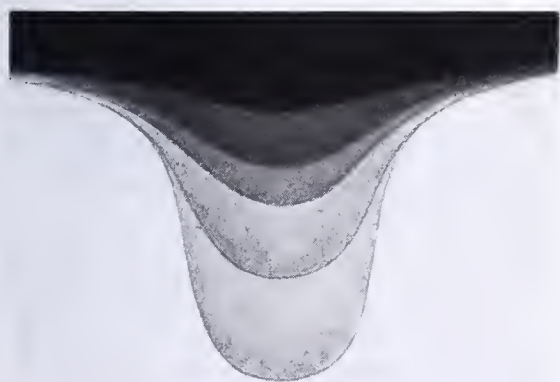


FIGURE 1. FORM OF DEPRESSION WITH SUCCESSIVE INCREMENTS OF AIR PRESSURE

Here the cell, *B*, which fits neatly between the blocks, *DD*, is mounted on a plate, *E*, to which a hinge, *H*, is attached at one end and a screw, *F*, at the other. By means of this screw it is possible to raise or lower the cell bodily and thus to bring the image of the undisturbed surface into coincidence with the telescope cross hair, set to the zero reading of the micrometer.

To facilitate cleaning, the cell is made out of a brass block, 10 mm. thick, from which a U-shaped portion has been removed. The glass plates forming the sides of the cell are simply held against the carefully machined sides of the brass block with small clamps (not shown).

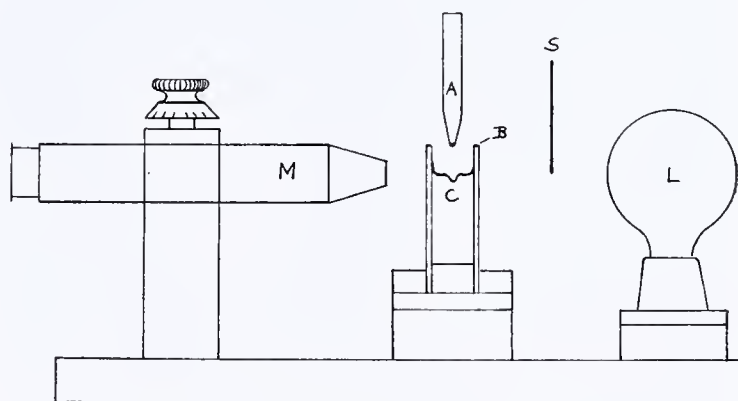


FIGURE 2. ARRANGEMENT OF APPARATUS

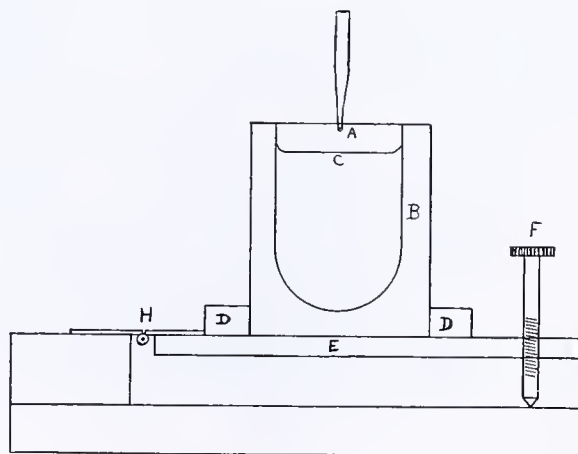


FIGURE 3. ARRANGEMENT FOR MAINTAINING CONSTANT SEPARATION BETWEEN JET ORIFICE AND LIQUID SURFACE

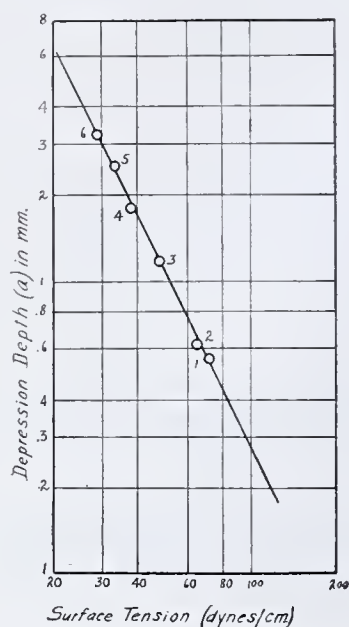


FIGURE 4. CALIBRATION CURVE, LIQUIDS OF KNOWN SURFACE TENSION

1, Water. 2, Glycerol. 3, Glycol. 4, Dibutyl phthalate. 5, Oil 104. 6, Oil 108.

For the sake of brevity, no description of the apparatus used in the production and maintenance of constant air pressure will be given. A pressure of about 2.4 cm. of water was found best. Calibration was effected by means of the known surface tensions of pure liquids—water, glycerol, glycol, dibutyl phthalate, and several mineral oils—no corrections being applied for density differences. The calibration curve obtained is shown in Figure 4, where the data are plotted on double logarithmic paper. The equation of this curve is

$$\gamma = Ka^{-1/2}$$

where γ is the surface tension, K a constant, and a the depth of the depression.

An advantage of the air-jet method over other methods is brought out in a study of temperature-surface tension relationships in oils used for the impregnation of cables. The specific case chosen for the sake of illustration relates to a mineral oil designated as No. 100/100. At 100° C. this oil had a viscosity of 0.5 poise and was therefore fluid; at 60° C., however, the viscosity has risen to 4 poises and the oil was thick. Surface-tension measurements made by the air-jet method and by the "Jolly balance platinum ring" method are in excellent agreement at temperatures above 60° C.

As shown in Figure 5, measurements by the platinum ring method become very erratic at 60°, only to become meaningless at lower temperatures. The jet method, however, is not subject to such limitations. Even at 25° C. where the oil would not pour—the viscosity having risen to 85 poises—the depression had reached a constant depth in 12 seconds and measurements could be carried out with the same ease.

This method is obviously applicable also to molten metals and to opaque materials in general. By directing a jet of pure nitrogen (in place of air) against the surfaces of molten bismuth and tin, it became evident that the surface tension of these materials is much greater than that of water. Up to the present time no entirely satisfactory method for measuring the depth of the depression has been found.

Another possible application of a modified jet method lies in the measurement of interfacial tension of water in contact with some nonmiscible, viscous liquid such as a heavy oil. In this case, a small, vertical jet of water, directed upward within the water and striking the oil-water interface perpendicularly, distorts the interface into a small hump or elevation whose height may be measured as before. Calibration

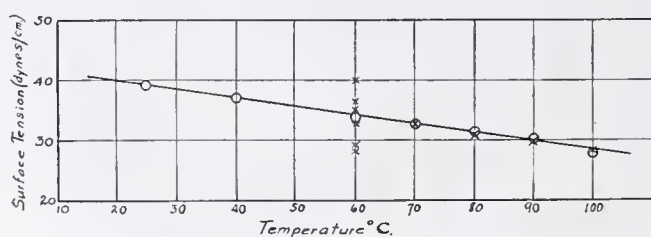


FIGURE 5. SURFACE TENSION vs. TEMPERATURE (MINERAL OIL 106)

xx Platinum ring-Jolly balance method
oo Air-jet method

may be effected through the use of liquids having higher fluidity and a known interfacial tension with water. In the absence of such information it is always possible to make measurements by creating electrically excited ripples (1) at the interface between water and nonmiscible liquids of high fluidity.

In connection with the preceding work it was noticed that air jets are extremely sensitive to short sound waves. If an air jet of the previously described type be directed vertically downward on a water surface—the separation between orifice and surface being 7.5 cm. and the pressure equal to 7.5 cm. of water—the depression immediately disappears as soon as a hissing sound is produced or if keys be rattled. There is a critical jet velocity and separation at which the sensitiveness is greatest. The behavior of the jet is therefore similar to that of the well-known "sensitive flame." The sensitive jet is well adapted for lecture-room demonstration: It is merely necessary to use a vertical projection lantern and to send the light through a flat-bottomed glass dish containing water. By focusing the water surface on the screen, it is found that a black spot appears where the water surface is deformed. This spot disappears immediately upon the production of short sound waves.

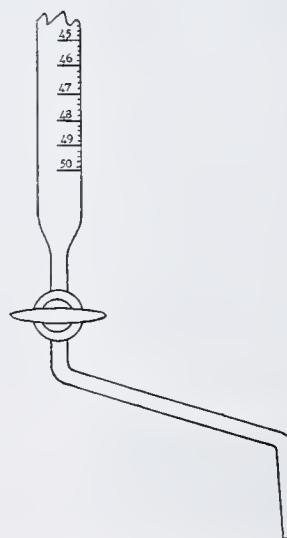
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- (1) Pfund, A. H., *Phys. Rev.*, **32**, 326 (1911).

RECEIVED November 1, 1935. Presented at the meeting of the Committee on Insulation (National Research Council) at Urbana, Ill., 1934.

A New Buret for Potentiometric Titrations

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THE burets which are commonly used for potentiometric titrations are usually the ordinary straight type or those which have the faucet type of stopcock. In many titrations where a stirrer, electrodes, and other apparatus are necessary in or above the titrating receptacle, it has been found convenient to use the buret herewith illustrated. It has the advantage of allowing control of the stopcock at a comfortable distance from the encumbering mechanism over the reaction vessel. Although the buret is not available from

laboratory supply houses, it can be easily constructed from the ordinary straight buret by anyone possessing a minimum of glass-blowing ability.

The tapered end of the stopcock tip is cut off at its base as far from the stopcock as possible. The stopcock is then wrapped with asbestos cord or other suitable protection afforded and a length of glass tubing having the same approximate dimensions is sealed on. The tube is then bent into the shape shown and the end drawn off to give a tapered point.

RECEIVED December 31, 1935.

Laboratory Service Testing of Automotive Lubricating Greases

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GREASE manufacturers in the United States produce annually nearly 300,000,000 pounds of lubricating grease, which is sold for approximately \$18,000,000. Of this total amount, 150,000,000 pounds of special grease, about 50 per cent, are consumed in automotive units. As in other industries, grease manufacturers are intently alert to new developments in mechanical engineering, particularly in the automotive field. This is only natural, since roughly one-half of the total amount of grease produced is consumed by the motorist.

Special service tests for automobile lubricating oils and gasoline have been more or less standardized, but the service testing of lubricating greases has been largely a matter of special technic developed as occasion necessitated by the grease manufacturer, automobile manufacturer, institution, or consumer. Because casual observation of service results in equipment on the road often leads to erroneous results and comparisons, laboratory service tests are frequently used to secure more precise data from which definite conclusions may

be drawn. In some cases, a series of greases differing only slightly in their usual properties must be studied to determine their relative service value. Road tests for thousands of miles might be needed to reveal practical differences, but accelerated laboratory service tests can be devised which enable definite comparisons to be made in a few hours.

Obviously, service tests may be used for proving

The importance and necessity of developing service tests of value in formulating improved automotive greases are emphasized in view of the grease industry's desire to meet more adequately the demands of modern cars, high-speed driving, and the consequent more severe lubrication conditions. Laboratory service tests have been devised which permit comparisons of service properties to be ascertained more quickly, economically, and precisely than in more laborious road tests. Road tests are, however, considered necessary for final evaluation of service properties.

color of the grease, odor, customer appeal, attractive appearance, and type of container, but performance must not be ignored. The discriminating purchasing agent, chemist, and engineer are frequently interested in knowing just how good a given lubricating grease is and how it performs in service.

Pressure-Gun Grease

Many of the cars on the road are equipped with some form of plain bushing shackle. In some cases, needle bearings

have been fitted into the king pins, and the development of "knee-action" front wheels has brought about modifications in steering mechanism bearings. However, the chief problem regarding the quality of pressure-gun greases is their ability to "stay in place." For this reason service tests for determining the retention characteristics of such greases have been developed by grease manufacturers and are of interest.

As with most lubricating grease problems, the viscosity of the mineral oil content, the consistency of the grease while being applied and while performing within the bearing, and the quality and amount of soap may all influence results obtained in service. For this reason, precise service tests for establishing the value of these items are very difficult. That much research remains to be done can be inferred from the fact that one finds on the market different gun greases manufactured with calcium, aluminum, and sodium soaps. Thus, the "experts," who in this particular case must be the grease manufacturers, do not agree. Perhaps a condition exists which is similar to that occurring in the food and clothing industries: that which pleases one is rejected by another for psychological reasons. Technically it should be possible to

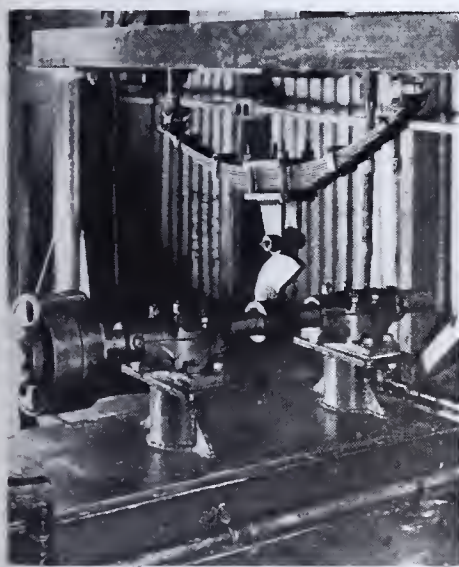


FIGURE 1. APPARATUS FOR DETERMINING RETENTION PROPERTIES OF PRESSURE-GUN GREASES IN SPRING SHACKLES

that under a given set of conditions one grease is superior to another. The time-honored tests for melting point, penetration, and per cent of water, soap, and ash, while of greatest value as control tests to secure uniform quality, leave too much to the investigator's imagination in predicting service performance. Carefully performed laboratory service tests are believed to be invaluable as indicators, pointing the direction in which definite improvements in automotive greases may be made.

Salesmanship must necessarily take into consideration



FIGURE 2. MODIFIED APPARATUS FOR DETERMINING RETENTION PROPERTIES

Produces more rapid vibration than device shown in Figure 1

TABLE I. PHYSICAL AND CHEMICAL TESTS ON COMMERCIAL PRESSURE-GUN LUBRICANTS

Lubricant Designation	Penetration at 77° F.		Dropping Point Ubbe- lohde	Kind of Soap	Ash %	S. U. Viscosity of Mineral Oil Content at 100° F.	Texture	Flow of Grease through Saybolt Universal Viscosity Tube		
	Unworked	Worked						35° F. G./min.	77° F. G./min.	100° F. G./min.
355 Al 400	...	385	89	Aluminum	..	400	Smooth	0.5	9.7	..
375 Ca 301	362	375	97	Calcium	1.04	301	Smooth
340 Ca 319	347	340	90	Calcium	1.06	319	Smooth
370 Ca 350	375	370	90	Calcium	..	350	Smooth
314 Ca 868	315	314	96	Calcium	1.61	868	Smooth
336 Ca 335	323	336	...	Calcium	..	335	Stringy	0.3	2.0	15.1
318 Ca 460	320	318	...	Calcium	1.34	460	Smooth	0.7	11.0	25.2
345 Ca 310	342	345	...	Calcium	1.7 max.	310	Smooth	1.4	19.8	..
354 Ca 315	354	354	...	Calcium	1.7 max.	315	Smooth	2.0	22.8	..
335 Al 290	325	335	...	Aluminum	..	290	Smooth	0.3	7.9	37.0
321 Ca 3000 (blown saponifiable oil)	316	321	90	Calcium	..	3000	Stringy	...	1.1	..
319 Ca 35 (latex)	309	319	88	Calcium	..	35	Stringy	...	0.2	..
227 Ca 300	207	227	92	Calcium	..	300
318 Ca 500 (poly-isobutylene)	...	318	95	Calcium	..	500
305 Ca 310 (milled)	305	305	91	Calcium	..	310	0.5	4.4	..
285 Ca 500 (latex)	...	285	95	Calcium	..	500	0.2	2.2	..
282 Ca 425	...	282	...	Calcium	..	425	0.3	5.0	..
350 Na 3100	...	350	135	Sodium	..	3100	Trace	1.1	..
450 Na 2500	...	450	...	Sodium	..	2500	Trace
390 Al 3000	...	390	101	Aluminum	..	3000	Trace
400 Al 1000 (app.)	...	400	...	Aluminum	..	1000
350 Al 1000 (app.)	...	350	...	Aluminum	..	1000
Oil 2000/100° F.	2000

determine which of two greases is best adapted to service in a given chassis bearing under given service conditions. However, the term "given service conditions" is a limitation which greatly restricts our general problem, and atmospheric temperatures, rain, dust, ice, wear, and design are variables which stand in the way of simplified service testing. The following method of testing has been worked out with a view to including the more normal types of operating conditions and thus forms the basis of opinions on retentivity as related to oil viscosity, consistency, type of soap base, and quantity of soap.

TESTING PRESSURE-GUN GREASES FOR RETENTIVITY. Either plain pin or screw-type shackle bolts have been adopted for the testing of pressure-gun greases in the apparatus shown in Figures 1 and 2 because they present the most important current shackle bolt lubrication problems. A model A Ford front spring with shackles and a Buick series 33-50 rear spring shackle, representing characteristic plain pin and screw-type shackle bolts, respectively, make it possible to study retentivity.

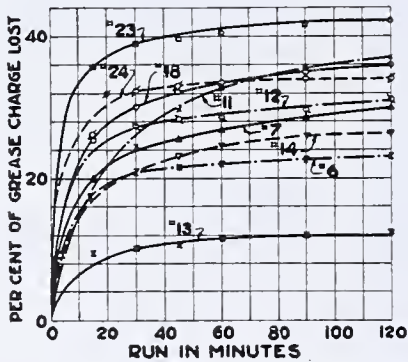


FIGURE 3. GREASE RETENTION TESTS
Front spring with plain bushing shackles on chassis lubricant tester. Charge, 2.80 to 2.90 grams of grease.

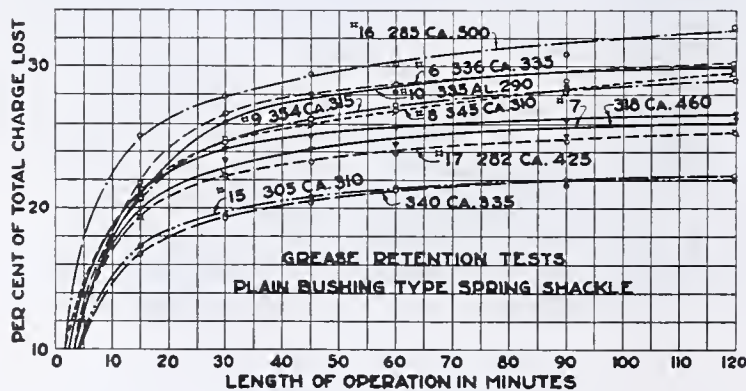


FIGURE 4

The actuating cam shown in Figure 1 was driven by a 3-horsepower electric motor through a 30 to 1 reduction gear. This mechanism imparts a 2.5-cm. (1-inch) deflection to the spring 60 times per minute. The cam is so designed that after maximum lift it leaves the roller follower and the spring returns freely to normal position. The deflection may also be obtained by means of a suitably designed cam as in Figure 2.

Before each test the spring shackles were completely disassembled and washed thoroughly with benzene, care being taken to remove all the old grease from the grease ducts and fittings. After thorough drying, the shackles and bolts were assembled, making certain that all interchangeable parts were replaced in the positions from which they were taken.

A small screw-type grease gun was filled with the grease to be tested and weighed on a balance to the nearest 0.05 gram. Each shackle was charged with grease until it showed signs of being forced out at the ends of the shackle bolt bushings. The filling gun was then reweighed and a small pad of cotton was used to wipe off the excess grease. The increase in weight of the cotton, subtracted from the loss of weight of the gun, gave the weight of grease charged to the shackle. The clearance between shackle and bushing was maintained at approximately 0.02 cm. (0.008 inch).

One form of grease-retention test consisted of taking a set of six readings during a 2-hour test period, the first four being taken at the end of 15-minute periods and the last two at the end of 0.5-hour periods. The readings were obtained by shutting the motor down and wiping the edges of the shackle bolts and bushings thoroughly with a weighed wad of cotton, and then measuring the increase of weight of the cotton.

An examination of Figures 3, 4, and 5 reveals that neither the kind of soap base, the viscosity of the oil content, the penetration value, nor slight variations in soap content alone

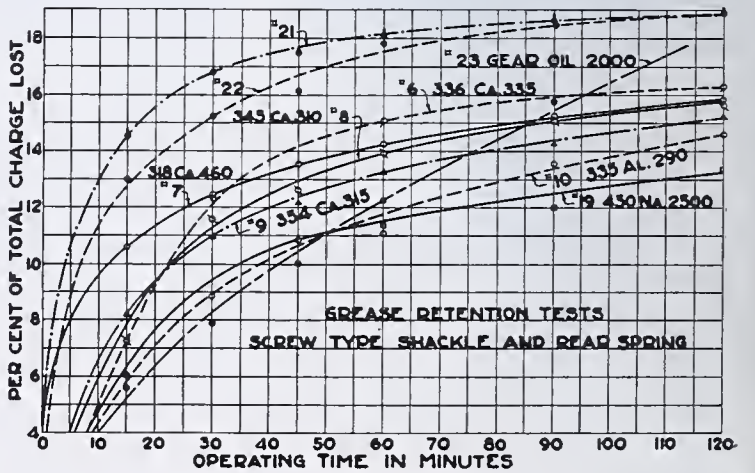


FIGURE 5

make one product better than another. Probably the combination of these factors and the modifying agents present which influence adhesion, aëration, and stability of the grease while in the shackles are the important items in determining the retentivity of a pressure-gun grease.

Grease 305 Ca 310 (Figure 4) shows a loss of 22 per cent in the 2-hour retention test (first number indicates worked penetration; second, soap base symbol; third, Saybolt Universal viscosity of oil content at 37.78° C., 100° F.). Grease 354 Ca 315 is similar with regard to penetration, type of soap, and mineral oil viscosity, but shows a loss of 28.8 per cent. A possible explanation of this difference is that the first grease has been milled to stabilize it, thus increasing its retentivity. It therefore may be concluded that the usual tests for penetration, soap base within certain limits, and oil viscosity do not accurately indicate the degree of retention which may be expected from a given pressure-gun grease. It also follows that further research towards establishing a correlation between retention, pressure viscosity, and stability of the grease film within the bearing are greatly needed.

RETENTIVITY OF PRESSURE-GUN GREASES IN PRESENCE OF WATER. In order to obtain information as to whether or not an aluminum stearate-base grease was more resistant to the action of rain water than a lime-base grease, the retention tester discussed above and shown in Figure 1 was equipped with a water-spray apparatus.

Alterations made in equipment consisted in the addition of a device for spraying water upon the shackles, and the building of a small tank about the apparatus to collect the water sprayed upon the shackles. The spray apparatus consists of two atomizers dipping into a tray of water. The two atomizers are operated by air under pressure, the intensity of the air jet being controlled through the use of an air valve and a pressure gage. The spray apparatus was placed in position so that a fine spray of water could be thrown up on the shackles.

Modifications of this device have undoubtedly been devised by others for splashing, dripping, or spraying water onto the shackles. The device as used is a simple method of obtaining a gentle washing action analogous to what might be met in service in stormy weather. The rebound of spray from the side of the tank and other parts of the apparatus results in water contacting the shackles from every direction from which water might come in actual service. The test conditions can also be fairly well reproduced by controlling the air pressure and the level of the water in the tray.

TABLE II. RETENTION OF GREASE

(Lubricant tester as shown in Figures 1 and 2, plain shackles, 2-hour test period, fine spray of water)

Kind of soap	Grease 335 Al 283	Grease 354 Ca 327	
	Aluminum	Calcium	
Per cent of soap	10.2	7.9	
Worked penetration	335	354	
Oil viscosity, S. U. at 100° F.	283	327	
Charge of grease, grams	2.81	2.81	2.88
Total water spray on shackles, liters	12.50	12.15	12.20
Water wiped from bearing surfaces and grooves, grams	0.141	0.235	0.302
Grease wiped from bearing surfaces and grooves, grams	0.160	0.149	0.179
Grease obtained by pressure-benzene treatment	1.241	1.320	1.302
Total grease retained, grams	1.401	1.469	1.481
Per cent retention	50	52	51

The spring, shackle bolts, and the crossbar from which the spring and shackles were suspended were assembled outside the tank which surrounds the lift cam. An excess of grease was forced through the Zerk fittings of the apparatus and measurements made as previously described.

A 2-hour test period was selected. This was consistent with previous tests carried out in the absence of water, in which the length of the test period was 2 hours. Except for

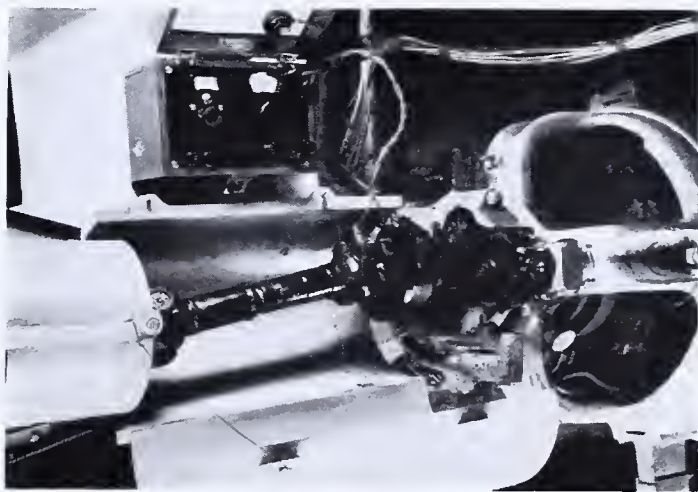


FIGURE 6. UNIVERSAL JOINT GREASE SERVICE TESTER, VIEWED FROM ABOVE

Electric dynamometer at right for absorbing power transmitted. Note method for determining temperatures within joints by means of thermocouples and shield for accumulating grease thrown from joint.

the spray playing on the shackles, the conditions of the test were identical with those of tests carried out on a dry basis. It was not possible to carry out observations on the amount of grease leaving the shackles at 15-minute or 0.5-hour intervals so as to obtain a retention-time curve.

The problem of recovering the grease from the water sprayed on the shackles was given consideration. However, this seemed impractical since the surfaces of the interior of the tank were large and the surfaces of the springs were irregular and likely to retain a certain amount of grease in crevices. The removal and measurement of the grease retained on the bearing was resorted to since the surface areas were smaller and easier to work with.

The results shown in Table II were obtained in the test.

The results on the two greases are in fairly close agreement, except in the amount of water removed from the shackles. However, these water figures are not very reliable, since losses are bound to occur through evaporation of water and probably also the loss of droplets of water from the shackles in removing shackle bolts. Neither grease showed any evidence of emulsification in the shackles as the result of the entrance of water.

The comparison between these two greases seems to be a fair basis for comparison of calcium- and aluminum-base chassis lubricants under wet conditions, since the oil viscosities, consistencies, and soap contents of the two greases were similar.

A complete investigation of the effect of water on shackle lubrication would of course include an investigation of screw-type shackles as well as plain shackles, and also the effect of different methods of bringing water in contact with the shackles. The effect of high-pressure washing should be of special interest in this regard. The effect of oil viscosity, soap content, and glycerol content on retention under wet conditions might also be investigated. However, since the results so far obtained show so little difference in the behavior of calcium- and aluminum-base greases in the presence of water, it is doubtful if much information of value would be obtained by further work on a comparison of aluminum- and calcium-base greases, although a comparison with sodium-base grease would no doubt be of interest.

Ordinarily, it is considered that temperature conditions met with in pressure-gun grease service are so low that high melting point soda-base greases are unnecessary. Since speeds and load are low, extreme pressure agents in most cases appear to be unnecessary.

Universal Joint Grease

Figure 6 shows a view of an apparatus used for service testing of universal joint greases. It consists essentially of two joints connected by an intermediate shaft, the entire assembly being driven by a 30-horsepower induction motor. Tests may be carried out at a speed of 3590 r. p. m. which corresponds to an approximate road speed of 80 miles per hour. The load transmitted was 20 horsepower and was absorbed by means of a 35-horsepower Sprague dynamometer. Conditions conducive to accelerated wear were provided for by operating the joints at an angle of 10°. Temperatures within the bearings were obtained by means of thermocouples and retention of the grease was studied and measured by collecting the grease thrown from the joints.

PENETRATION. Table III shows that very little relation exists between penetration and the temperatures attained within universal joints. Sample 4 has a fairly low unworked penetration value of 205, and the temperature rise within the universal joint was 19.5° C. (35° F.). Universal joint grease 7 was much softer, having an unworked penetration value of 325, yet the temperature rise was 27.8° C. (50° F.). Universal joint grease 6 is somewhat heavier than 7, but the lower penetration value of 275 apparently did not cause any significant difference in the bearing operating temperature which remained at 50° above atmospheric. It is therefore concluded that from the standpoint of service the penetration of a

universal joint grease is not of paramount importance. It is fully realized that consistency and viscosity must be taken into consideration in dispensing greases at low temperatures. A range of 300 to 330 worked penetration should be satisfactory for purposes of manufacturing control.

PERCENTAGE OF WATER. Most commercial universal joint greases contain less than one per cent of water, and while it appears that the moisture content has no direct bearing on efficacy of lubrication, it is felt that a good grease should not contain more than 1.5 per cent of water. At very low temperatures, greases containing no glycerol and much water might be found objectionable.

MELTING POINT. Inasmuch as the service tests indicate no definite advantages for No. 5 and No. 7 high melting point greases, particularly from the standpoint of bearing temperatures and wear, the point is not especially important if service characteristics alone are taken into consideration. If a high melting point were indicative of good grease retention, we should expect No. 5 and No. 7 to be considerably less subject to leakage. An examination of Table III will indicate that the opposite of this is true. We therefore conclude that, from the standpoint of service, melting point specifications are not essential providing the greases are well-made products having soda-soap bases.

FREE ALKALI. The analysis indicates that grease 5 has a free acid content of 0.42 per cent. However, the corrosion test (copper strip, 3 hours at 100° C., 212° F.) was satisfactory

TABLE III. RESULTS OF SERVICE TESTS MADE WITH A SPICER UNIVERSAL JOINT

(Type G, plain bearing joint)

Sample	Max. Op. Temp. above Housing ° F.	Fe ₂ O ₃ in Universal Joint after Test Gram	Throw-Off 30 Hours ^a Grams	Pressure Viscosity ^b G./min.	Viscosity of Oil, Saybolt Seconds at 100° F.	Soap %	Penetration Cone at 77° F. ^c	MacMichael No. 24 Wire at 95° F. ^c
1	30 ¹	0.157 ³	65.0 ⁶	869 ⁵	657 ⁷	14.1	299	180
2	31 ²	0.198 ⁶	62.5 ⁵	949 ⁶	1032 ⁶	11.4	345	100
3	34 ³	0.133 ³	60.0 ³	544 ³	247 ³ Fur.	8.2	304	160
4	35 ⁴	0.245 ⁷	67.0 ⁷	602 ⁴	745 ¹ Fur.	14.2	204	Not detd.
5	38 ⁵	Trace ¹	58.8 ²	342 ²	1986 ⁵	7.8	310	Not detd.
6	50 ⁶	0.117 ²	54.5 ¹	230 ¹	295 ²	18.5	275	Not detd.
7	50 ⁷	0.143 ⁴	61.8 ⁴	602 ⁴	2072 ⁴	7.8	325	Not detd.

Exponents indicate relative standing.

^a 100-gram initial charge.

^b 30 lb. per sq. inch at 140° F.

^c Unworked.

TABLE IV. ANALYTICAL DATA ON COMMERCIAL UNIVERSAL JOINT GREASES

Grease No.	1	2	3	4	5	6	7	8	9
Physical Properties:									
Appearance	Granular and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Stringy and dark green	Dark green
Odor	Sweet	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy
Melting point, ° C., Gillette	72	59	49	86	50	80	62	66	Liquid
Melting point, ° C., Ubbelohde	130	82	151	167	143	126	153	143	Liquid
Channel test, ° F.	25	15	30	80	15	30	20	25	10
Penetration at 77° F., unworked	205	310	275	325	310	...
Penetration at 77° F., worked	320	325	330
MacMichael, viscosity No. 24 wire at 95° F.	180	100	160
Corrosion, copper strip, 3 hrs. at 212° F.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.
Bleeding test, 1 hr. at 175° F.	No sep.	No sep.	No sep.	No sep.	No sep.	No sep.	No sep.	No sep.	...
Separation test at 220° F.	None	None	None	None	None	...
Separation test at 250° F.	None	None	None	...	Slight
Composition, per cent by weight:									
Soap	14.1	11.4	8.2	14.2	7.8	18.5	7.8	7.9	8.0
Moisture	0.70	0.65	0.1	0.60	0.7	1.5	0.55	0.45	0.6
Oil	85.0	86.0	91.0	86.0	90.7	80.3	91.0	92.5	91.6
Free alkali (or acid)	0.35	Neutral	0.42	0.42	0.7
(oleic acid)
(NaOH)	0.03	0.01	0.26	0.06	0.24	0.04	0.09	0.43	0.01
Asphaltic material	0.14	0.37	0.26	0.06	0.24	0.04	0.07	0.43	0.01
Sulfur	0.49	0.82	0.96	0.34	0.89	0.32	0.36	0.64	0.45
Ash:									
Per cent by weight	2.61	2.09	1.50	2.59	1.44	3.68	1.61	1.47	0.89
Analysis, per cent of ash:									
Na ₂ CO ₃	95.4	92.2	87.2	87.4	82.1	95.2	82.8	87.6	...
Na ₂ SO ₄	4.3	5.5	11.5	9.0	12.2	4.1	8.6	10.9	...
Fe ₂ O ₃	1.0	1.1
Al ₂ O ₃	2.9
CaO	0.4	...	0.5	...	2.0	0.2	2.3	0.9	95.0
Acid-insoluble and Fe ₂ O ₃	0.9	1.1	0.8	4.0	0.9	...
Mineral oil:									
Viscosity, S. U. at 100° F.	657	1062	247 Fur.	745 Fur.	1986	295 Fur.	2072	1060	2810
Viscosity, S. U. at 210° F.	65	66	109.6	156	102	153	111	66.0	128
Gravity, ° A. P. I.	22.4	17.4	19.7	20.9	20.3	23.7	20.8	17.4	19.0
Flash, ° F.	400	395	415	465	405	515	335	365	405

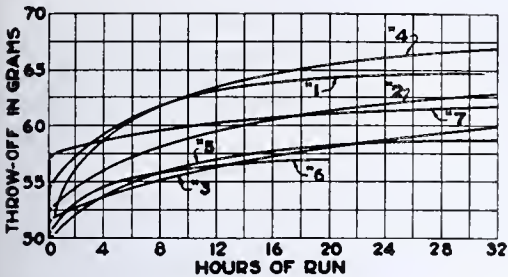


FIGURE 7. REJECTION OF LUBRICANT BY SPICER PLAIN BEARING UNIVERSAL JOINT, TYPE G

Speed 3590 r. p. m., 10° angularity between faces. Original charge 100 grams of lubricant

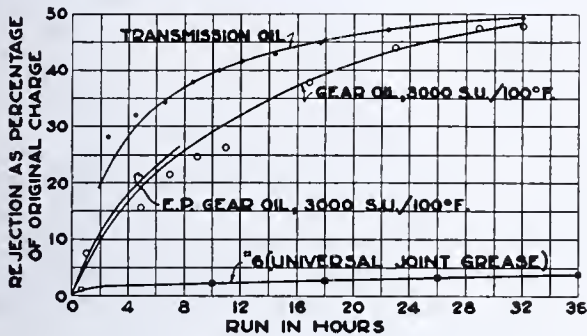


FIGURE 9. REJECTION OF LUBRICANT FROM SPICER NEEDLE-BEARING UNIVERSAL JOINT, TYPE KRL

Speed 3590 r. p. m., load 20 h. p. Universal joint charged with lubricant to 7.5 grams

and, since wear in the service test was exceedingly low for this product, it must be concluded that the free acid content of even this amount is not a serious disadvantage. While these service tests have not been carried out with the particular view of ascertaining the practical significance of free alkali and free acid, the results obtained are such that no particular service disadvantages could be predicted on the basis of these qualities. Therefore the free alkali and free acid specifications appear to have no very useful purpose with regard to service.

FILLERS. It is the writer's belief that no grease recommended for universal joint lubrication should contain any appreciable quantity of filler, as inert solid materials would greatly accelerate wear.

ASH. The ash content is some indication as to the percentage of soap present in the grease. Since the soap content does not correlate at all well with retention properties, it cannot alone be taken as an indication of serviceability. It will

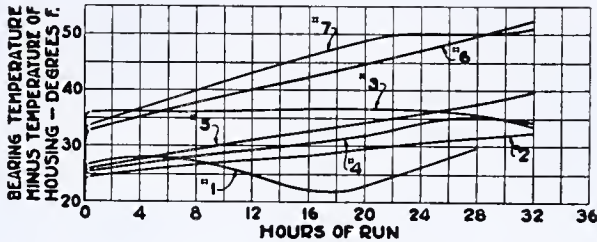


FIGURE 8. TEMPERATURE INCREASE IN SPICER TYPE G UNIVERSAL JOINT

Speed 3590 r. p. m., 20 h. p., 10° angularity

be observed from Table III that universal joint grease 5, containing only 7.8 per cent of soap, lost 58.8 per cent in 30 hours of operation, as compared with 54.5 per cent for No. 6, containing 18.5 per cent of soap. This difference in retention properties is not proportional to the difference in soap percentages. Again, universal joint grease 1, a nationally advertised product which was found to be lost from the joint to a greater extent than any of the other products tested, contains only 4.4 per cent less soap than No. 6 which had the best retention properties. Therefore, the necessity for specifying the ash or soap content is not at all apparent when considering service results. It is obvious that in order to conform to definite penetration ranges an adequate soap content must be utilized by the grease manufacturer. The fact that the ash content may vary within fairly wide limits does not appear to have a serious effect on service results.

CORROSION. None of the commercial universal joint greases investigated failed to meet the copper-strip corrosion test.

MINERAL OIL. What has been said above with regard to soap content can also be applied to the percentage of mineral oil used for compounding universal joint lubrications. Slight variations in soap content and consequently oil content are not reflected in the service results.

TESTS WITH NEEDLE-BEARING UNIVERSAL JOINTS. Gear oils and semi-fluid gear greases of the types recommended by the manufacturers of the needle-bearing trunnion universal joints are rejected at a rate some ten times greater than that of a grease such as No. 6, while the operating temperatures are substantially the same in each case. At the end of 32 hours' testing, with each of the lubricants used, the rejection curve showed that little further rejection was probable, and that ample lubricant remained in the bearings.

Lubrication failure for needle joints appears possible only through careless assembly or damage to the cork seals, regardless of mileage run.

During the test period which exceeded 10,000 miles the wear on the bearings was negligible. The fine-lapped finish of the bearing pins did not acquire a full polish during this time.

Figure 9 presents the performance of the greases tested in a clear form, showing especially the low throw-off of universal joint grease 6 with its satisfactory operating temperature.

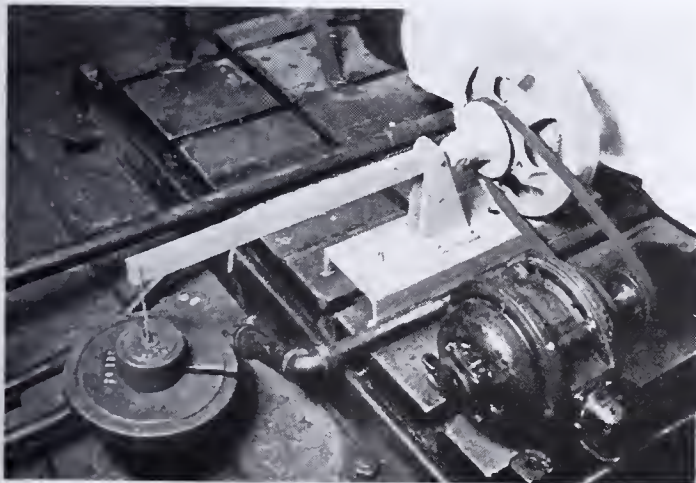


FIGURE 10. GENERAL ARRANGEMENT OF LABORATORY APPARATUS FOR MAKING SERVICE TESTS ON WHEEL BEARING GREASES

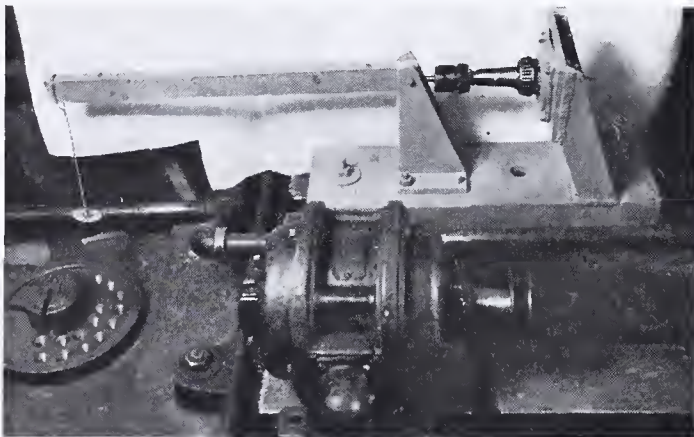


FIGURE 11. WHEEL BEARING GREASE TESTER SHOWN IN FIGURE 10

Disassembled to show method of applying axial load by means of the weight and lever system. Note thermocouple leads to bearing.

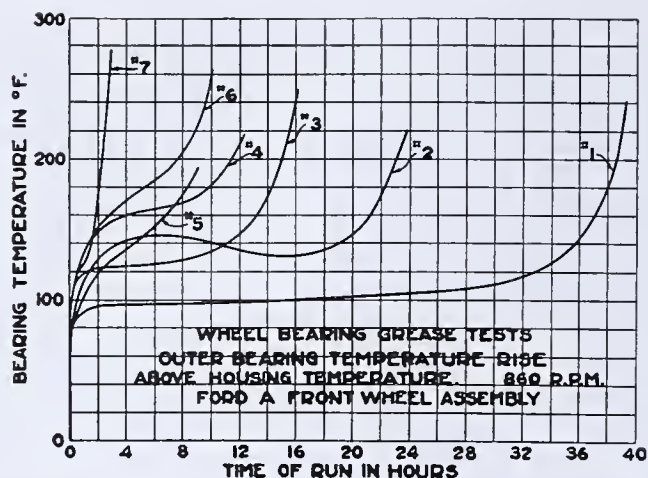


FIGURE 12. WHEEL BEARING TEMPERATURE INCREASES

Load, 7580 pounds

Because the performance of universal joint grease 6 was so satisfactory in service tests, it is concluded that a grease is preferable to an oil.

Wheel Bearing Greases

A service testing device which has been utilized successfully consisted of a front wheel hub and spindle assembly from a model A Ford car. The arrangement of this spindle and the mechanism employed for loading the bearings in an axial direction are shown completely in Figure 10. An axial load of 1336 pounds is produced by a weight of 30 pounds at the end of the lever arm. This is equivalent to producing a total radial load of 7580 pounds on the bearing. Obviously, this load of 7580 pounds is greatly in excess of the normal load which a Ford front axle is required to carry, although shock loads may be even higher. The hub is operated by means of a 0.5-horsepower motor producing a speed of 860 r. p. m. This is equivalent to a road speed of approximately 80 miles per hour. Both the loading and speed are considerably in excess of normal conditions for a car operating on the road. This, however, was considered necessary in order to produce accelerated tests.

Thermocouples were placed under the inner race of both spindle bearings and enabled fairly accurate temperatures to be obtained with the bearings in service. The entire wheel bearing grease tester was enclosed in a thin metal housing in order to avoid sudden fluctuations in temperature due to drafts. New outer bearing cones and races were used for each test run. After thoroughly cleaning the bearings with aviation gasoline, they were carefully packed with 10 grams of the sample of grease to be tested, the grease being kneaded into the spaces between the Timken tapered rollers and their separator. Later tests indicate that one of the patent bearing packers would accomplish accurate results.

Temperature readings for the bearings were made hourly and at the same time the housing and atmospheric temperatures were recorded. Following these hourly temperature readings, the driving motor was stopped and the apparatus disassembled for inspection. Care was taken to disturb the grease as little as

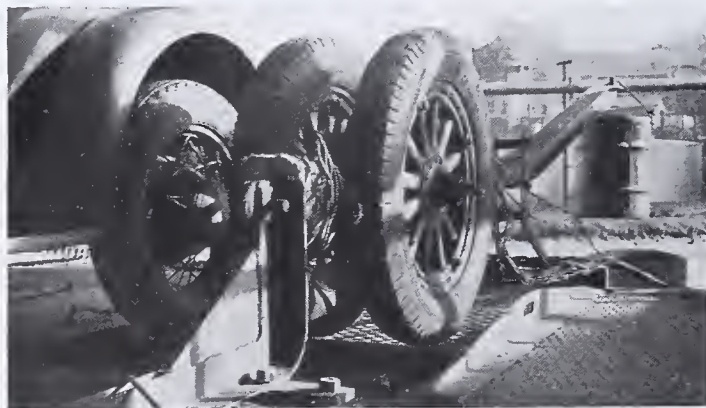


FIGURE 13. CHASSIS DYNAMOMETER ATTACHMENT FOR MAKING WHEEL BEARING GREASE TESTS IN LOADED FRONT WHEELS

Heat supplied by electric resistance coils to simulate conditions of braking

possible. Observations of the oil films and the color of the surfaces of the rollers and races were made at this time, and particular attention was paid to any changes in the character of the grease. The tendency of the grease to leak from the bearing was also noted.

RESULTS OF TESTS. The relative ratings of the wheel bearing greases tested are summarized in Table V. The best product tested is given an arbitrary value of 1 and that which is considered most unsatisfactory has been assigned a value of 7.

TABLE V. TEST OF WHEEL BEARING GREASES

Grease	Time to Reach High Temperatures Hours	Temperature Rise ° F.	Appearance of Roller Bearing	Retention of Grease	Final Rating
1	(1) 39	(1) 250	1	1	1
2	(2) 24	(2) 220	3	2	2
3	(3) 16	(3) 250	1	3	3
4	(4) 12	(5) 220	6	4	4
5	(5) 9	(4) 200	3	5	5
6	(6) 10	(6) 260	3	6	6
7	(7) 3	(7) 275	7	7	7

The temperature-time relationship obtained for the several greases tested is shown more clearly in Figure 12 than is indicated in Table V where the time to reach an objectionably high temperature is variable as well as the rise above the atmospheric temperature. Grease 1 was found to be definitely superior in all the qualities observed.

The analyses of the wheel bearing greases tested are shown in Table VI. The following brief comments deal with the laboratory tests made on the greases investigated and discuss the formulas and usual chemical laboratory tests.

PENETRATION. Grease manufacturers are not in general agreement as to whether worked or unworked penetration values should be established. Table VI shows wheel bearing greases having variations in unworked penetrations ranging from 155 for grease 8 to 240 for grease 9. The worked penetration values range from 197 to 316. Information from other sources indicates that the consistency of commercial wheel bearing greases may vary from a worked penetration value of 170 to values as high as 300. It is realized that worked penetration values are more significant from the standpoint of service than corresponding unworked penetrations. For a satisfactory grease there should be no objection to establishing a worked penetration range of 210 to 240.

PERCENTAGE OF WATER. In general, the water content of wheel bearing grease at present used throughout the country will vary from a trace to as much as 1.8 per cent. The effect of these variations in water content has not been conclusively demonstrated in the service tests which the author has conducted. It is felt that the presence of appreciable quantities of water is of little significance and it has been found that the experimental grease, containing as much as 1.1 per cent of water, produces no objectionable corrosion or discoloration of used grease or bearing surfaces. A high water content may tend to increase corrosion and wear, although this has not been definitely proved. In order to reduce the tendencies in this direction, 0.1 per cent of a material to inhibit corrosion has been added to grease 1. Practical tests have shown that in the presence of this ingredient the water content may reach rather high percentages without detrimental effects to the bearings. A maximum water content of 1.5 per cent is a good working value.

MELTING POINT. It will be observed from Table VI that Ubbelohde dropping points vary from 100° C. for grease 7 to 200+° C. for grease 4. A study of dropping points in connection with service results and retention in wheel bearings has not conclusively demonstrated that a minimum specification as high as 180° C. is definitely necessary. In view of the fact that field and laboratory service tests have not resulted in noticeable leakage when operating on wheel bearing grease 1 having an Ubbelohde dropping point of 145° C., a minimum

TABLE VI. ANALYTICAL RESULTS ON WHEEL BEARING GREASES

Grease No.	1	2	3	4	5	6	7	8	9	10
Physical tests:										
Appearance	Bright black Spongy	Brown Slt. Stringy	Green black Stringy	Green brown Stringy	Light brown Stringy	Bright green	Gray brown	Dark green Granular Stringy	Dirty brown Soft Stringy	Brown Granular Stringy
Odor	E. P. base	Fatty	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy	Soapy and like nitro-benzene	Sweet-pungent
Dropping point, ° C.										
Gillette	100+	80	100+	...	97
Ubbelohde	145	180	162	200+	133	162	100	138	129	139
Unworked penetration at 77° F.	164	204	199	198	159	155	240	189
Worked penetration at 77° F.	232	236	...	225	280	236	197	...	316	310
Separation test at 250° F.	None	...	None	None	None	None	None	None	None	None
Corrosion, 3 hrs. at 210° F.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.
Composition, per cent by weight:										
Water	1.4	...	1.4	0.1	1.75	0.45	1.8	1.0	1.8	1.1
Oil	80.3	83.5	79.0	78.5	72.0	79.5	81.0	73.0
Soap	19.9	16.4	19.0	18.8	23.5	18.4	17.2	22.0
Free alkali as NaOH	0.04	Neutral	0.19	0.12	0.02	0.18	0.05 as Ca(OH) ₂	0.13	...	0.11
Free acid as oleic	0.07	...
Ash:										
Per cent by weight	2.86	...	4.14	3.20	3.41	4.02	2.60	3.90	2.95	4.30
Analysis, per cent of ash:										
Na ₂ CO ₃	89.8	93.3	97.2	89.6	...	95.7	96.9	94.1
Na ₂ SO ₄	7.0	3.4	2.0	8.5	...	2.8	3.4	3.9
R ₂ O ₃	2.2	1.0	0.2	1.5	1.6	1.3	Ca ₂ SO ₄	Na ₂ SO ₄
CaO	1.0	0.2	0.4	0.3	96.2
Mineral oil:										
Viscosity, S. U. at 100° F.	348 Fur.	1254	330	282 at 130°	355	803	1867	1440
Viscosity, S. U. at 210° F.	179 app.	...	66.1	76.0	50.3	72.2	52.1	63.7	90.4	81.8
Gravity, ° A. P. I.	22.2	21.1	23.9	25.4	22.1	20.9	19.6	20.2

TABLE VII. PERFORMANCE CHARACTERISTICS OF STEERING GEAR LUBRICANTS

Lubricant	Mechanical Efficiency				Timken Wear ^a Mg.	Timken Film Strength ^b O. K.	Heat Stability at 220° F.	Separation at 220° F.	Retention ^c %
	Buick gear, -40° F. Stat. %	Dyn. %	% Efficient, 150° F. Stat. %	Dyn. %					
1	24.0	13.0	75.0	77.0	34.4	8,575	11,430	Jells	4.8
2	31.0	16.0	73.5	76.0	24.9	7,140	10,000	Jells	3.0
3	0 Solid	0	80.0	79.5	31.2	14,280	17,140	Becomes hard	1.15
4	71.0	55.0	76.5	79.7	..	14,280	17,140	O.K.	9.2
5	27.0	8.0	73.5	77.5	9.8	22,860	25,700	O.K.	8.9
6	62.0	36.0	76.2	78.0	8.2	17,140	18,570	O.K.	3.5
7	68.0	62.0	70.0	76.5	..	14,280	17,140	Oil separates	5.65
8	68.0	15.0	73.5	76.0	..	2,900	5,714	Oil separates	3.8

^a 6 hours at 100 feet per minute, 40,000 lb. per sq. inch.
^b 400 feet per minute, lb. per sq. inch.
^c Per cent of charge lost.

Ubbelohde dropping point of 135° C. (275° F.) appears to be justifiable.

PERCENTAGE OF FREE ALKALI AND FREE ACID. There should be no objection to a maximum free alkali value of 0.6 per cent and a maximum free acid value of 0.3 per cent, but many bearing manufacturers specify much closer ranges. It is felt, however, that there should be no difficulty in maintaining wheel bearing greases at a point much nearer to neutral than is indicated by these rather wide ranges. From the standpoint of service, however, there are no indications that products having extreme values within these ranges will be objectionable under actual service conditions.

PERCENTAGE OF FILLERS. It is generally agreed that any good wheel bearing grease should contain no appreciable quantities of inert fillers, as these materials will act as lapping compounds and cause increased wear.

PERCENTAGE OF ASH. Reference to Table VI reveals that the soap contents of the wheel bearing greases investigated vary from 16.4 to 23.5 per cent. The best service results were obtained with grease 1, having a soap content of 19.5 per cent. In general, the ash values are proportional to the percentage of soap. However, appreciable deviations in the ash content are not considered as having any particular influence on the serviceability of the grease. It is therefore apparent that a maximum ash content of 5 per cent could be readily met by most grease manufacturers and there is no need for meeting rigid specifications established at appreciably lower values. From the standpoint of control and uniformity, however, complying with the above suggested worked penetration

ranges would serve in a better manner than making ash tests on all batches of wheel bearing grease.

CORROSION. None of the greases investigated was found to be unsatisfactory when subjected to the 3-hour copper strip corrosion test carried out at 100° C. (212° F.). While it might appear that there is no necessity for including a specification of this kind in view of the general high quality of greases in this respect, it is felt that, since wheel bearing greases



FIGURE 14. INNER RACE OF TAPERED ROLLER-TYPE WHEEL BEARING

Showing results of overloading and improper lubrication

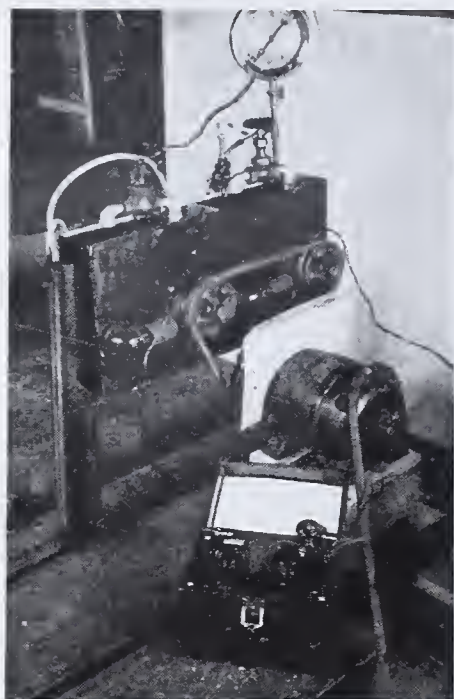


FIGURE 15. LABORATORY APPARATUS FOR DETERMINING SERVICE CHARACTERISTICS OF AUTOMOTIVE WATER-PUMP GREASES

Temperature of cooling fluid, rate of flow, and discharge pressure of pumps are easily controlled.

cussed under the heading of "Percentage of Ash." Wheel bearing grease 7 has been prepared with a calcium base and in service tests has been given a rating of 7, and from all considerations was the most objectionable product investigated. Not emphasized in Table V is the fact that leakage for grease 7 was many times that of any of the other greases tested. It is significant that all of the other greases were manufactured with soda-soap bases.

Water-Pump Grease

A laboratory service testing device, making use of Chevrolet or other makes of water pumps, is shown in Figure 15. By selection of a motor pulley of suitable size, pumpshaft speeds may be

may contain sulfurized materials and other "extreme pressure" bases, the corrosion test is of importance. There is some evidence from the field that soda-soap base wheel bearing greases are corrosive when a small amount of water gains entrance to a bearing. For this reason, the addition to soda-soap greases of traces of compounds which inhibit corrosion seems justified.

SOAP. The question of soap content has been dis-

attained of 500 to 2000 r. p. m. Water at temperatures up to 100° C. (212° F.) or various antifreeze mixtures which may have a detrimental effect on the lubricating film are placed in the rectangular metal boxes on the sides of which the pumps are mounted. Practical tests and comparisons of the abilities of greases to resist the displacing action of the various solutions can be made.

Prolonged tests with various makes of pump packing, in which the packing gland is kept abnormally tight, yield results bearing on the characteristics of grease and packing most desirable for preventing shaft scoring. With this device it is also possible to gain information as to the quantity of grease which may find its way into the cooling system and retard heat transfer. The investigation with this equipment has not yet been completed.

Steering Gear Grease

Eight steering gear lubricants were subjected to a series of tests to determine their qualities in four essential respects: efficiency, wear, stability, and retention. The efficiency and retention tests were applied over a temperature range from -40° to 82.22° C. (-40° to 180° F.).

The tests were mostly of a conventional nature, but attention is drawn to the separation test at 104.44° C. (220° F.) which is regarded as being significant. The aluminum-soap greases (No. 1, No. 2, and No. 3) heated to this temperature either jell or solidify, and the calcium-soap lubricants (No. 7 and No. 8) separate and do not recombine on cooling. The sodium-soap lubricants (No. 15, No. 18, and No. 6) are heat-stable. The test temperature of 220° F., while appreciably higher than temperatures which have been observed in service, is not unreasonably so and has been employed to cover extreme cases.

EFFICIENCY. A steering gear lubricant tester was constructed, as shown in Figure 16, in such a way that two gears could be held at controlled temperatures and the ratio of steering wheel effort to steering arm torque could be determined. The gears tested were a Saginaw worm and roller type made for Buick cars and representative of steering gears used by General Motors for 1934, and a Gemmer worm and sector type as used on the 1934 Ford. Gears of these types are estimated to be on 30 and 62 per cent, respectively, of 1932-34 cars. Large inspection

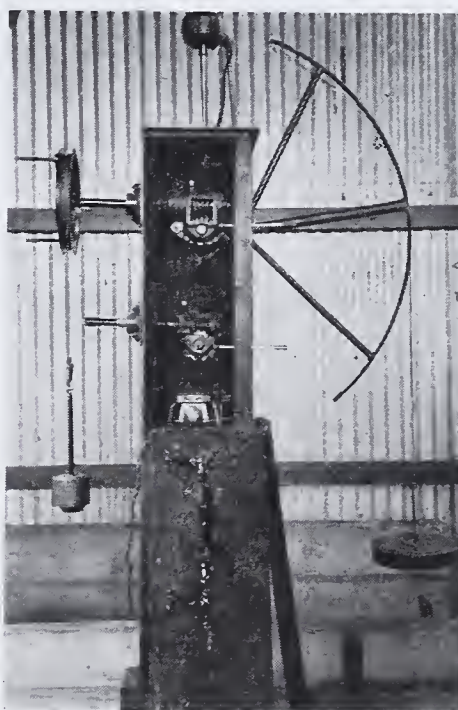


FIGURE 16. APPARATUS FOR DETERMINING STATIC AND DYNAMIC EFFICIENCIES OF STEERING GEARS

Front removed to show arrangement of gears

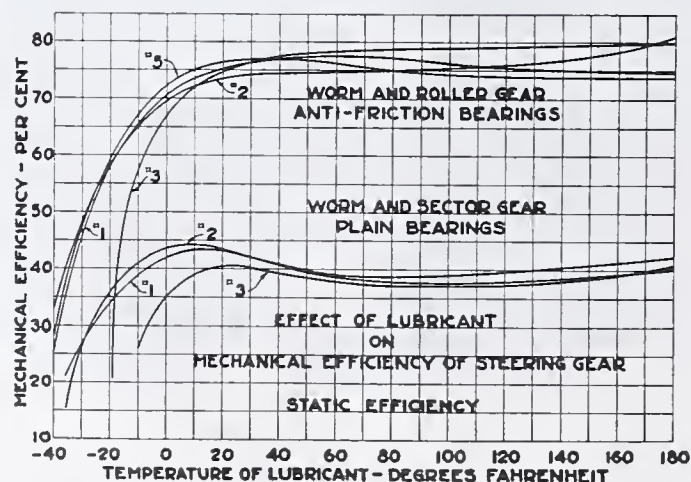


FIGURE 17

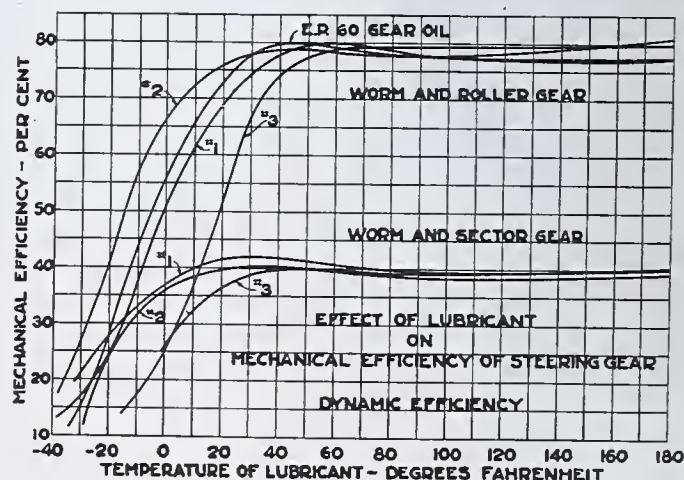


FIGURE 18

TABLE VIII. ANALYTICAL DATA: STEERING GEAR LUBRICANTS

Sample No.	1	2	3	5	6	7	8	9
Physical tests:								
Appearance	Green brown Stringy	Black viscous Liquid	Black Semi-solid	Black Liquid	Brown stringy Semi-solid	Light brown Semi-solid	Brown Semi-solid	Dark green Brown
Odor	Pine tar	Sharp-soapy	Soapy	Pungent	E. P. base	E. P. base-soapy	Fatty	Sharp-soapy
Dropping point								
Gillette, ° C.	36	Room temp.	76	Liquid	Room temp.	42	50	Liquid
Ubbelohde, ° C.	48	78	92	Liquid	126	78	81	Liquid
Pour point, ° F.	50	60	Above 120	-5	5	Too heavy	Too heavy	30
Channel test, ° F.	0	10	10	-10	Below 0	0	0	10
MacMichael, 1-cm. bob, 60 r. p. m.	No. 26 wire 140 at 75° F.	No. 26 wire 65 at 70° F.	No. 24 wire 126 at 80° F.	No. 26 wire 33 at 76° F.	No. 26 wire 56 at 80° F.	No. 26 wire 55 at 70° F.	No. 26 wire 143 at 70° F.	No. 26 wire 93 at 80° F.
Corrosion, copper 3 hr., 212° F.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.
Bleeding test, 175° F., 1 hr.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.	O.K.
Separation test, 220° F.	Jells	Jells	Becomes hard like axle grease	No separation	No separation	Grease breaks down	Separates	Slight separation
Composition, per cent by weight:								
Soap	10.2	7.3	8.7	4.6	2.9	5.6	7.1	8.0
Moisture	0.1	0.1	0.2	0.15	0.1	0.4	0.2	0.6
Oil	85.9	92.2	79.8	93.5	97.1	92.5	90.0	91.6
Free alkali or fatty acid	4.1 oleic	3.6 oleic	11.2 oleic	Pb present	0.01 NaOH	0.14 oleic	0.21 oleic	0.7 oleic
Asphaltic material	2.0	0.3	2.0	0.32	Trace	0.01
Sulfur	0.33	0.50	0.83	2.00	1.86	2.47	0.40	0.45
Ash:								
Ash, %	3.08	0.77	1.78	3.3	0.35	0.77	0.86	0.89
Analysis, %	14.0 Na ₂ CO ₃ 69.3 PbO 13.8 PbSO ₄	77.2 Al ₂ O ₃ 21.6 Na ₂ CO ₃	80.1 Al ₂ O ₃ 7.3 Al ₂ SO ₄ 6.9 Na ₂ CO ₃	90.0 PbO 0.9 Acid-ins.	90.0 Na ₂ CO ₃	62.2 CaO 9.8 Al ₂ (SO ₄) ₃	91.6 CaO 6.4 Na ₂ CO ₃ 2.8 Fe ₂ O ₃	80.5 CaO 19.6 CaSO ₄ 3.7 Fe ₂ O ₃
Mineral oil:								
Color	Green black	Black	Black	...	3-Red	Red-blue	8	Brown-black
Viscosity, S. U. at 100° F.	1667	2000	3270	2640	314	548	379	2810
Viscosity, S. U. at 210° F.	89.4	118	164	135	49	53.9	51.4	128
Gravity, ° A. P. I.	20.5	21.9	19.7	16.8	23.2	20.2	22.5	19.0
Flash, ° F.	405	285	390	345	375	320	370	405

Sample No.	10	11	12	13	14	15	16	17
Physical tests:								
Appearance	Green brown Liquid	Black Liquid	Black Green	Black Brown	Green Semi-solid	Dark green Brown	Black	Green Semi-solid
Odor	Sweet soapy	Phenol-like	Sour	Faintly soapy	Slightly soapy	Pine tar	Nitrobenzene	Sweet
Dropping point								
Gillette, ° C.	Liquid	Room temp.	Liquid	Liquid	54	Liquid	Liquid	Room temp.
Ubbelohde, ° C.	Liquid	Liquid	Liquid	Liquid	84	Liquid	Liquid	64
Pour point, ° F.	30	50	60	-5	100	15	-0	20
Channel test, ° F.	15	..	40	-10	25	5	-5	0
MacMichael, 1 cm. bob, 60 r. p. m.	No. 26 wire 180 at 80° F.	No. 26 wire 50 at 70° F.	No. 26 wire 100 at 80° F.	No. 26 wire 15 at 80° F.	No. 26 wire 154 at 70° F.	No. 26 wire 14 at 80° F.	No. 26 wire 14 at 80° F.	No. 26 wire 113 at 70° F.
Corrosion, copper 3 hr., 212° F.	...	O.K.	O.K.	Not O.K.	O.K.	O.K.	O.K.	O.K.
Bleeding test, 175° F., 1 hr.	...	O.K.	O.K.	O.K.
Separation test, 220° F.	Solidifies	No separation	Solidifies	No separation	No separation	No separation	No separation	No separation
Composition, per cent by weight:								
Soap	6.6	1.2	6.3	3.5	5.5	3.7	3.1	5.2
Moisture	0.2	0.05	0.2	0.1	0.2	None	Trace	0.1
Oil	92.2	98.3	90.5	95.5	84.0	95.6	97.0	92.0
Free alkali or fatty acid	Al ₂ O ₃ pres.	0.6 oleic	0.56 oleic	Lead present	0.03 NaOH	0.35 oleic	0.21 oleic	1.1 oleic
Asphaltic material	0.03	0.1	0.2	0.5	...	0.2	0.1	...
Sulfur	0.28	0.95	0.99	2.33	0.37	2.37	5.76	2.47
Ash:								
Ash, %	0.86	0.04	0.08	0.37	1.02	0.03	0.005	0.97
Analysis, %	85.6 Al ₂ O ₃ 8.4 Al ₂ (SO ₄) ₃	No analysis	No analysis	34.2 PbO 51.3 PbSO ₄	80.0 Na ₂ CO ₃ 9.6 Na ₂ SO ₄ 2.5 Fe ₂ O ₃	No analysis	No analysis	59.6 Na ₂ CO ₃ 38.4 Na ₂ SO ₄ 2.2 Fe ₂ O ₃
Mineral oil:								
Color	Green red	Brown black	Green	Black	Green black	Green black	...	Dark green
Viscosity, S. U. at 100° F.	2298	4520	4560	1267	3930	1305	...	1097
Viscosity, S. U. at 210° F.	120	230	218	92	177	87	...	65.4
Gravity, ° A. P. I.	21.8	21.6	23.7	18.6	23.2	20.7	...	17.5
Flash, ° F.	420	390	530	390	490	415	...	410

holes were made in the casings of the gears for convenience in changing lubricants and were closed by plates. Thermometers were inserted directly into the lubricant by means of packing nuts. The gears were set to factory adjustments at the beginning of the series of tests and were not subsequently altered.

Temperatures down to -40° F. were secured by carbon dioxide snow condensed in a chamois-skin bag formed around the gear housing, and those up to 180° F. were secured by means of a hot plate and a fan for circulating the warm air in the cabinet. Observations on actual cars with atmospheric temperature ranges up to 105° F. showed that temperatures in steering gears in service seldom exceed 160° F.

The efficiency tests were conducted by hanging a 50-pound weight from the quadrant representing 1350 inch-pounds, or a condition intermediate between turning the wheels while stationary and turning at 10 miles per hour. This was regarded as typical of the effort applied when parking in a crowded street. It was then determined what weight needed to be added to the input pulley to secure the first movement of the steering arm (static efficiency) and also to secure a rate of movement of 10° in 5 seconds (dynamic efficiency). Static efficiency measurements were made in the middle of the worm only and dynamic

efficiency measurements were made in three positions. The steering arm moves through about 90° in the case of both gears and dynamic efficiency tests were run in the central position and 15° on either side of this.

Preliminary experiments showed that tests made in this manner gave the same average results as tests at 10° intervals over the whole range. The dynamic and static efficiencies were found to be nearly equal at all temperatures where the lubricant was fluid, but at low temperatures the dynamic efficiency was much lower than the static—that is, initial movement of the gears was secured with less effort than was necessary for a continuous movement of 2° per second. This corresponds to about 36° per second on the steering wheel or moderately rapid turning.

The results obtained are shown in Figures 17 and 18.

RETENTION. Observations were made on the retention characteristics of the lubricants by collecting the leakage at high temperatures from 15.56° C. (60° F.) upwards. Some of

this leakage was due to the method of mounting the gears, and the figures are much higher than would be found in practice. However, the relative figures show what may be expected with gears in poor mechanical condition.

FILM STRENGTH AND WEAR TESTS. Film strength determinations were made on the Timken machine at rubbing speeds of 400 and 100 feet per minute, and wear tests, also on the Timken machine, were carried out for a duration of 6 hours at 40,000 pounds' pressure and a speed of 100 feet per minute. The 40,000 pounds' pressure is at first sight above the film strength pressure at 100 feet per minute for some of the lubricants, but these pressures are nominal, assuming line contact, and actual unit pressures after a run-in period will be considerably less than this. No actual failures of lubrication occurred during the wear tests.

Table VII summarizes the significant performance characteristics of the most important of the lubricants tested.

Lubricant 6 is exceeded in dynamic efficiency at low temperatures only by No. 7, which is unsatisfactory from the point of view of heat stability, and by No. 4 which is consider-

ably inferior from the point of view of retention. Its wear characteristics were good and its retention was exceeded only by No. 3, which gave a poor efficiency at low temperatures and unsatisfactory heat stability.

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Determination of Starch in Plant Tissues

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OF THE various methods that have been proposed to determine the starch content of plant tissues, only those which depend upon the estimation of the sugar produced by hydrolysis of the starch with dilute acid or with enzymes have received much attention in recent years. Sullivan (15) has recently reviewed and discussed the whole problem of starch determination, and has pointed out the unreliability of most methods that have been suggested. Denny (5) has carefully compared the results with several procedures, and has shown that hydrolysis of prepared tissue with takadiastase, even under the best conditions, may lead to serious error owing to the inclusion of substances other than starch which are hydrolyzed by this enzyme preparation with the production of sugar. He has therefore emphasized the desirability of extracting the starch from the tissue with some suitable solvent as a step preliminary to its isolation and subsequent hydrolysis to sugar.

Even this procedure, in the authors' experience, may not entirely eliminate contaminating sugar-yielding substances, and it has, accordingly, seemed desirable to base the estimation of starch in plant tissues upon a more specific reaction for this substance—namely, the well-known color reaction with iodine. A procedure of this kind was described in 1895 by Dennstedt and Voigtländer (4), but was found unreliable by Littleton (8) and by Witte (17). Occasional references to the application of the iodine-starch reaction for quantitative purposes are to be found in the literature (9), but no satisfactory analytical development appears to have been made.¹

The method described in the present paper is designed to be applied to samples of dry plant tissue.

The powdered material is prepared for analysis by thorough extraction with 75 per cent alcohol, and is then ground either by hand or in a special ball mill to an extremely fine powder. The starch is extracted from a suitable sample either by 21 per cent hydrochloric acid at 20° to 22° C. (Rask's method, 11) or by concentrated calcium chloride solution at 100° C., the solvents being applied repeatedly until no further starch is removed. The starch is then precipitated at the correct acid reaction and salt

concentration by means of iodine-potassium iodide reagent, the precipitate is decomposed with alcoholic alkali, and the starch is isolated as such. It is then dissolved in water with the aid of acetic acid, and a definite excess of iodine is added as potassium iodide-iodate mixture. The starch-iodine compound remains in colloidal solution under these conditions, and the intensity of the light transmitted through an S-61 (red) filter is read in a Zeiss Pulfrich spectrophotometer against a control solution containing the reagents alone. The quantity of starch present is calculated from a calibration curve prepared by subjecting known quantities of highly purified potato starch to the same procedure.

The method gives results that can be duplicated within 10 per cent on quantities of the order 0.1 to 0.2 mg. and within 3 per cent on quantities between 1 and 3 mg. of starch.

Reagents

Calcium chloride solution: 216 grams of Baker's c. p. anhydrous calcium chloride dissolved in 250 ml. of water. The hot solution is filtered through asbestos and is kept in a warm place; concentration approximately 46 per cent by weight.

Hydrochloric acid (Rask's acid): 247 ml. of concentrated hydrochloric acid diluted to 500 ml.; concentration approximately 21 per cent.

Hydrochloric acid 2.3 *N*: 100 ml. of concentrated hydrochloric acid diluted to 500 ml.

Acetic acid 2 *N*: 57 ml. of glacial acetic acid diluted to 500 ml.

Sodium hydroxide 10 *N*: 420 grams of sodium hydroxide diluted to 1000 ml.

Alcoholic sodium hydroxide 0.25 *N*: 25 ml. of 5 *N* sodium hydroxide, 320 ml. of 95 per cent alcohol diluted to 500 ml.

Sodium chloride 20 per cent: 20 grams of pure sodium chloride diluted to 100 ml.

Iodine-potassium iodide: 30 grams of iodine and 50 grams of potassium iodide diluted to 250 ml.

Potassium iodide 10 per cent: prepared in small quantities and discarded when it becomes yellow.

Magnesium carbonate: c. p. grade containing very little free alkali.

Thymol blue 0.04 per cent: prepared according to Clark (3).

Potassium iodate 0.01 *N*: 0.1783 gram of pure potassium iodate diluted to 500 ml.

Of these reagents, the potassium iodate alone needs to be prepared with quantitative accuracy.

Preparation of Tissue

Green plant tissue is rapidly dried in a ventilated oven, provided with a fan and baffles to circulate the air over the tissue,

¹ The paper of Sullivan (16) which describes a method based upon precipitation with iodine and subsequent hydrolysis of the starch to sugar, came to hand after this manuscript had been submitted for publication.

at 70° to 80° C., and is then ground to pass a 50- to 60-mesh sieve. Weighed samples of from 2 to 5 grams are continuously extracted in paper thimbles with 75 per cent alcohol for at least 6 hours, the residues are dried and weighed, and are then ground in a mortar or, preferably, in a small ball mill until the powder will pass through fine silk bolting cloth.

A convenient ball mill can be readily improvised from quarter-pint cream bottles closed by rubber stoppers. A cylindrical block of wood that contains four evenly spaced holes bored parallel to the axis, and of such size as to accommodate the bottles snugly, is mounted on an axle constructed of 0.6-cm. (0.25-inch) pipe attached firmly to the block and carefully centered. The axle is set in bearings held by clamps, and the cylinder is rotated by a belt from a laboratory motor around the cylinder or suitable pulley attached to the axle. About 45 0.6-cm. (0.25-inch) steel ball bearings are added to each bottle with the sample, and the mill is rotated at 120 revolutions per minute for about 8 hours.

Extraction of Starch

HYDROCHLORIC ACID METHOD OF RASK. It is convenient to carry out the extraction of four samples simultaneously; 0.200-gram samples of the ground tissue are weighed into 25 × 200 mm. heavy-walled Pyrex test tubes, and 1.5 grams of sharp sand, 5 cc. of water, and a stout glass stirring rod are added to each. The tubes are placed in a boiling water bath for 15 minutes to gelatinize the starch, the contents being vigorously triturated from time to time with the rod. The tubes are cooled to 10° C. and 5 ml. of concentrated hydrochloric acid are slowly added, the temperature being kept below 22° C. The contents are then ground with the rod over a period of about 10 minutes, each tube being treated for about 0.5 minute at a time and kept in a water bath at 20° C. during the intervals. The rods are then rinsed off with a few drops of Rask's acid and the tubes are centrifuged for 1 minute. The supernatant fluid is decanted into 25 × 200 mm. test tubes calibrated at 50 ml., allowing sufficient time for drainage, and the lips are rinsed with a little water; these tubes are kept in a water bath at 10° to 15° C.

The centrifuged residues are next ground with the rods for about 0.5 minute each, and 3 ml. of Rask's acid are added, the alternate grinding of each tube being continued as before for 5 to 7 minutes. The tubes are then centrifuged and the residues are extracted twice more in the same manner, the successive extracts being collected in the graduated test tubes. A few drops of the fourth extract are tested with a drop of 0.01 *N* iodine solution, and if a definite blue color is observed a fifth extract is made. Finally the residues are washed by grinding once with 10 ml. of water.

The combined extracts are made to 50 ml. with water and are then kept in a refrigerator until the next step in the analysis is undertaken; they are stable under these conditions for at least 72 hours.

CALCIUM CHLORIDE METHOD. Samples of 0.200 gram of tissue are weighed out into test tubes as before and 0.05 gram of magnesium carbonate, 1.5 grams of sharp sand, 5 ml. of water, and a stirring rod are added to each. The tubes are heated with occasional trituration in a boiling water bath for 15 minutes and 7 ml. of the concentrated calcium chloride reagent, previously heated in the same bath, are added. The four tubes are then ground successively, while in the boiling water bath, for 0.5 minute each over a period of about 10 minutes. The rods are rinsed

with a few drops of water, the tubes are centrifuged, and the extracts are collected in 25 × 200 mm. test tubes graduated at 50 ml. The residues are ground for 0.5 minute each, are returned to the boiling water bath, and 3 ml. of water and 5 ml. of hot calcium chloride solution are added to each. The alternate grinding is continued for about 8 minutes, when the tubes are again centrifuged. Two more successive extracts are made in the same manner. A few drops of the fourth extract are acidified with dilute hydrochloric acid and tested with a drop of 0.01 *N* iodine solution; if a blue color is obtained a fifth extraction with calcium chloride is made. The residues are finally washed by being stirred with 5 ml. of water and centrifuged. The combined extracts are made to 50 ml. volume and are kept in the refrigerator.

Precipitation of Starch Iodide

The proper size of aliquot of the starch extract to be taken for analysis can readily be determined after a little experience by removing 0.2 ml. and testing with a drop of 0.01 *N* iodine solution. If a light blue color is obtained, 10 ml. of the extract should be used; if an intense blue, 5 ml. or less. Calcium chloride extracts must, of course, be acidified before testing.

The aliquots are transferred to Gradwohl-Plavais sugar tubes and are diluted to 10 ml.; 2 drops of 0.04 per cent thymol blue and a slim stirring rod with an enlarged end are placed in each.

HYDROCHLORIC ACID EXTRACTS. The tubes are cooled to 10° C. in a bath and 10 *N* sodium hydroxide is added drop by drop with constant stirring to a faint blue color, then 2.3 *N* hydrochloric acid to a yellow color and 1 ml. in excess. The temperature must not be allowed to rise above 25° C. If the aliquot is less than 5 ml., 2 ml. of 20 per cent sodium chloride are added and finally the starch is precipitated by the addition of 0.5 ml. of concentrated calcium chloride

and 6 to 10 drops of iodine-potassium iodide reagent. The calcium chloride is necessary in order to produce a precipitate which, on decomposition with alcoholic sodium hydroxide, will yield a granular precipitate of starch—without it this precipitate is gummy.

CALCIUM CHLORIDE EXTRACTS. If the aliquots are smaller than 5 ml., 1 ml. of calcium chloride is introduced. The acidity is adjusted as already described, 2 ml. of 20 per cent sodium chloride are added, and the starch is precipitated with 6 to 10 drops of iodine-potassium iodide.

The subsequent procedure is identical for both acid and calcium chloride extracts. The tubes are allowed to stand for 10 minutes and are then lightly stoppered or covered with glass bulbs and immersed in a boiling water bath for 15 minutes. After being cooled to room temperature, any precipitate floating on the surface is broken up with a small rod and the tubes are centrifuged. It is usually impossible to decant the supernatant fluid from these precipitates. The best method is to draw it off with a long thin capillary tube attached to a suction flask and source of vacuum with light-walled rubber tubing so that the rate of flow can be instantly controlled. By this means floating particles are usually caught on the walls of the tube and the fluid may

Starch is extracted from plant tissues either by hot concentrated calcium chloride solution or by cold 21 per cent hydrochloric acid, and is precipitated from the extract by means of iodine at the correct acidity and salt concentration. The iodine precipitate is decomposed with alcoholic alkali, and the starch is isolated as such, dissolved in dilute acetic acid, and converted again to the iodine compound under conditions in which it remains in colloidal solution. The light transmission is read in a Pulfrich spectrophotometer and the quantity of starch present is calculated from a calibration curve constructed from observations on pure potato starch.

The method has been applied to a number of plant tissues. The results, in general, are lower than those obtained by calculation of the starch from the sugar reduction obtained after hydrolysis, but are believed to be more trustworthy. It has been found that, in many cases, sugar-yielding substances contaminate the isolated starch and give rise to interference.

The method is highly specific and gives results duplicable within 3 per cent on quantities of starch between 1 and 3 mg. in the aliquot analyzed and within 10 per cent on quantities as small as 0.1 mg.

be removed to less than 1 ml. As a rule floating particles consist of sublimed iodine, and their loss does not affect the analysis. The precipitates are washed twice successively with 2-ml. portions of 60 per cent alcohol, the precipitate being mixed with the wash fluid by gentle shaking of the tube which is then thoroughly centrifuged. Spattering of the precipitate on the walls of the tube must be avoided.

Decomposition of Starch Iodide

To the packed precipitates, 2 ml. of alcoholic sodium hydroxide are added and the precipitates are triturated with glass rods until nearly colorless. The rods are then washed with 60 per cent alcohol, and the decomposition is completed by heating the tubes in a bath at 70° to 80° C. for 5 minutes with gentle agitation. The tubes are cooled and centrifuged, the fluid is decanted from the starch, and this is washed twice with 2 ml. of 60 per cent alcohol. After the last washing the tubes are inverted and allowed to drain thoroughly.

Estimation of the Starch

The starch precipitates are treated with 5 ml. of water and are heated with frequent shaking for 5 minutes in a boiling water bath. After being cooled, 0.5 ml. of 2 *N* acetic acid is added, and the contents of the tubes are thoroughly mixed and centrifuged. The fluids are decanted into 25 × 200 mm. test tubes, calibrated at 20 and 50 ml., immersed in a water bath at 15° C. The residues are washed by being agitated with 3 ml. of water, and are centrifuged.

The solutions of starch are treated with 2 ml. of 2 *N* acetic acid, 0.5 ml. of 10 per cent potassium iodide, and 5 ml. of 0.01 *N* potassium iodate, all being exactly measured. Two compensating solutions are simultaneously prepared that contain 8 ml. of water, 2.5 ml. of 2 *N* acetic acid, 0.5 ml. of 10 per cent potassium iodide, and 5 ml. of potassium iodate. The two compensating solutions are diluted to 20 and 50 ml., respectively. The unknowns are diluted to either 20 or 50 ml., depending on the intensity of color developed, and are allowed to stand, after being thoroughly mixed, for 5 minutes. The extinction coefficient of each solution is then determined in the Pulfrich spectrophotometer using the compensating solution of the same volume on the control side of the instrument, and the equivalent of starch is calculated from the calibration curve. The quantity found is referred to the 0.200-mg. sample of prepared tissue and this in turn corrected for the loss in weight during the preparation of the original dried tissue for the starch analysis.

It will be found that the 50-ml. dilution should be used for quantities in excess of 0.5 mg. of starch, the 20-ml. dilution for smaller amounts. Cells should be selected of such length that the readings fall between 20 and 80 per cent transmission.

Reference Standard and Calibration of Instrument

In order to obtain from the extinction coefficient the actual quantity of starch present, it is necessary to calibrate the instrument in terms of a reference standard of pure starch. For this purpose, a high grade of potato starch was selected. This was thoroughly extracted with a mixture of ether and alcohol and with water, and was then dried in the air. Analyses of two different lots so treated gave moisture contents of 11.36 and 4.78 per cent, ash contents of 0.29 and 0.30 per cent, and no nitrogen. The two specimens therefore contained 88.4 and 94.9 per cent of starch. Calculation of the starch content by means of the factor 0.93 from the sugar reduction after hydrolysis with 0.7 *N* hydrochloric acid for 2.5 hours gave 87.4 and 94.4 per cent. The values obtained for the organic solids were therefore taken to represent the starch content of these samples with sufficient accuracy. Both were used in the preparation of the calibration curve.

Standard solutions of starch in hydrochloric acid were obtained by treating the equivalent of 0.050 gram of dry starch as already described for the extraction of starch from tissue. To prepare solutions in calcium chloride, the equivalent of 0.050 gram of starch, 0.05 gram of magnesium carbonate, and 5 ml. of water were heated in a boiling water bath for 15 minutes and 15 ml. of calcium chloride solution were added. A few drops of caprylic alcohol and a few angular quartz pebbles were introduced and the solution was boiled under reflux for 2 hours. The solution was then diluted with 15 ml. of water, transferred to a 25 × 200 mm. test tube calibrated at 50 ml., diluted to the mark, and centrifuged.

Aliquots of these solutions that contained 0.1 to 3.0 mg. of starch were then carried through the procedure already described, with particular attention to the addition of salts previous to the precipitation with iodine. Determinations were also made on solutions in calcium chloride that were heated for longer times both at 100° C. and at the boiling point. Furthermore, the precipitation with iodine was carried out in the cold and at 100° C., in the presence of acetic acid and also of hydrochloric acid, and finally the readings of the color were made at various temperatures from 15° to 28° C. All results were duplicable within 5 per cent in spite of these variations. The data were found to yield satisfactorily straight lines between the limits 0.1 and 0.6 mg. of starch read at 20-ml. volume, and between the limits 0.2 and 3.0 mg. of starch at 50-ml. volume. Accordingly, all the data were assembled and the best straight lines for the two volumes were obtained by the method of least squares. The data for these lines are shown in Table I.

TABLE I. CALIBRATION DATA FOR STARCH DETERMINATION
(Filter S-61; 1-cm. cell)

Starch Mg.	Volume Ml.	Extinction Coefficient
0.100	20	0.069
0.200	20	0.133
0.500	20	0.343
0.200	50	0.053
0.500	50	0.133
1.00	50	0.278
2.00	50	0.559
3.00	50	0.840

Comparison of Colorimetric with Hydrolytic Method on Pure Starch

Samples of standard starch solution both in calcium chloride and in hydrochloric acid were carried through the procedure described up to the isolation of the starch precipitate, save that the iodine precipitates were not heated but were allowed to stand at room temperature for 30 minutes.

The precipitated starch was treated with 2 ml. of 0.7 *N* hydrochloric acid and the tubes, covered with glass bulbs, were heated in a boiling water bath for 2.5 hours. After completion of the hydrolysis, the solutions were cooled and neutralized to phenol red with 0.5 *N* sodium hydroxide. They were then diluted to 10, 15, or 20 ml., depending on the quantity of starch present, and aliquots were analyzed for reducing sugar by the Shaffer and Somogyi (14) method (copper reagent No. 50 containing 1 gram of potassium iodide).

In addition, samples of dry starch were hydrolyzed directly, and also after having been dissolved in calcium chloride and precipitated with alcohol, or simply dissolved in hydrochloric acid. The glucose values are summarized in Table II.

TABLE II. YIELD OF GLUCOSE FROM POTATO STARCH

	Glucose %	No. of Determinations	Factor
Direct analysis of starch	106.8 ± 1.0	8	0.936
Solution of starch (CaCl ₂ or HCl)	99.2 ± 2.0	7	1.008
Solution of starch in either solvent precipitated with iodine	99.2 ± 2.0	14	1.008

Starch on direct analysis yields 106.8 per cent of glucose, but, after having been dissolved in either of the two solvents, yields 99.2 per cent and the yield is unchanged by precipitation with iodine. It is clear therefore that the empirical factor 0.93, long in use to convert glucose yield into starch, does not apply if the starch has been taken up in either of these solvents. This factor is based upon the experiments of a number of early investigators (6, 10).

The factor 1.01 calculated from the present experiments on starch solutions suggests that there may have been incomplete solution of the sugar-yielding material, but tests of the trace

of residue left after solution of the starch in the solvent showed that it gave no blue color with iodine and can therefore not be what is ordinarily understood as starch. Inasmuch as the present method to determine starch depends on the blue coloration, it is necessary to define starch for our purposes in terms of this reaction, and to correlate the results of the colorimetric method with the glucose yielded by starch after the starch has been treated with solvents.

The yield of glucose from starch that has been precipitated by iodine varies materially according to the temperature and acidity at which the precipitation is made, although neither factor has much effect upon the color value. Data that illustrate these points are shown in Table III. Equal samples of starch solutions were precipitated with iodine at room temperature and one sample was then heated to 100° C. as described. The acidity at which the precipitations were conducted was also varied. Examination of the data shows that the colorimetric values were not affected by heating at any of the acidities tested. The glucose values were, however, seriously reduced if the iodine precipitate was heated in the presence of mineral acid.

TABLE III. COMPARISON OF COLORIMETRIC AND SUGAR METHODS ON RECOVERY OF PURE STARCH

Acid per 15 Ml. of Neutralized Starch Solution	Starch, Colorimetric		Starch from Sugar Titration, Glucose × 1.01	
	Room tempera- ture		Room tempera- ture	
	100° C.		100° C.	
	Mg.	Mg.	Mg.	Mg.
Acetic acid 5.0 N, 0.3 to 0.5 ml.	0.095	0.099	0.092	0.097
	2.03	2.02	1.98	1.96
	2.00	2.03	2.00	2.00
	2.02	2.00	1.97	1.98
Hydrochloric acid 2.3 N, 0.5 ml.	2.04	1.68
Hydrochloric acid 2.3 N, 2.0 ml.	2.04	2.00	1.98	1.32
	2.00	1.97	2.00	1.20
	1.03	1.00
	1.00	1.05
Hydrochloric acid 2.3 N, 2.6 ml.	1.01	1.02
	0.098	0.093
	0.095	0.104
	2.00	1.22
Hydrochloric acid 2.3 N, 5.2 ml.	1.99	1.01

It might be inferred from these data that precipitation in the presence of acetic acid in the cold is preferable to the procedure here recommended. As will be shown below, however, in the practical application of the method to plant tissues, the precipitation of interfering substances is to a large extent avoided by the technic the authors have adopted.

Starch Determination in Plant Tissue

BEHAVIOR OF CALCIUM CHLORIDE EXTRACTS. A solution of pure starch in concentrated calcium chloride is not stable at room temperature for more than 48 hours, the amount of starch precipitable by iodine slowly diminishing. Dilution with 10 volumes of water gives a solution which is even less stable, notable losses of starch frequently being observed within 24 hours.

Losses of starch also occur during the process of extracting starch from plant tissues with hot calcium chloride unless steps are taken to control the acidity. The calcium chloride solutions the authors have used were faintly alkaline to phenolphthalein. After being heated with plant tissue, they rapidly became more acid and marked losses of starch occurred if the reaction was allowed to drop below pH 6.0.

Table IV shows the effect upon the apparent starch content when samples of leaf tissue are heated with calcium chloride alone and together with calcium or magnesium carbonate. The extracts were made by heating 0.5 gram of dry tissue at 100° C. for 17 hours with 5 ml. of water and 10 ml. of calcium chloride; from 0.1 to 0.2 gram of the carbonates was used in addition where mentioned. The extracts were diluted to 50 ml. and the reaction was determined at the quinhydrone

electrode; starch analyses were then carried out on suitable aliquots.

TABLE IV. EFFECT ON RECOVERY OF STARCH OF HEATING TISSUE WITH CALCIUM CHLORIDE AT DIFFERENT REACTIONS

(Extractions at 100° C. for 17 hours)			
Tissue Used		Reaction of	Starch
		Final CaCl ₂ Solution	
		pH	%
Tobacco leaf E		3.06	0.00
Tobacco leaf E	+ CaCO ₃	4.99	0.58
Tobacco leaf E	+ 2.0 per cent of starch	3.06	0.00
Tobacco leaf E	+ MgCO ₃	6.93	1.88
Tobacco leaf E	+ 2.0 per cent of starch + MgCO ₃	6.94	4.00
Tobacco leaf H		3.10	0.00
Tobacco leaf H	+ MgCO ₃	7.32	0.14
Tomato leaf		4.45	0.30
Tomato leaf	+ CaCO ₃	4.90	0.61
Tomato leaf	+ MgCO ₃	6.96	2.17

Complete loss of starch took place if the reaction was not controlled. Calcium carbonate in the quantity used was ineffective in maintaining a relatively neutral solution and serious loss of starch occurred. Magnesium carbonate, however, preserved a neutral solution and permitted complete recovery of the starch.

Although an unusually long period of heating was employed in these experiments in order to magnify the results, appreciable loss may occur from tobacco leaf tissues during extraction of starch as described above, unless magnesium carbonate is added. The losses were small, however, with salvia or alfalfa leaf tissue.

The authors have recommended extraction with calcium chloride at 100° C. rather than at the boiling point of the concentrated solution (113° C.). A careful comparison of starch values obtained by successive extractions at the boiling point and at 100° C. showed that somewhat lower results were obtained at the higher temperature. Data that illustrate this and also give a comparison with cold hydrochloric acid extraction are shown in Table V.

TABLE V. COMPARISON OF EXTRACTION OF STARCH BY BOILING CALCIUM CHLORIDE SOLUTION, BY CALCIUM CHLORIDE AT 100° C., AND BY HYDROCHLORIC ACID

Tissue Used	CaCl ₂ 113°-114° C.	CaCl ₂ 100° C.	HCl 20° C.
	%	%	%
Tobacco leaf E	1.55	1.65	1.60
Tomato leaf	1.43	1.43	1.45
Tomato stem A	9.95	10.65	10.60
Tobacco stem H	0.73	0.76	0.78
Tobacco stem K	4.23	4.70	4.63
Tobacco stem J	1.73	1.81	1.88
Tobacco stem I	1.60	1.65	1.68

It is clear that the cold hydrochloric acid extraction method is to be preferred to extraction with calcium chloride at the boiling point. The stability of hydrochloric acid extracts for considerable periods of time (5), provided they are stored in a refrigerator, is also a point in favor of this method of extraction and for most purposes the authors prefer it.

ILLUSTRATIVE DATA. Tables VI and VII show data that illustrate the close reproducibility of starch determinations in various plant tissues, and the accuracy with which starch can be recovered when added to a starch-free tissue. It will be noted that 0.2 mg. of starch in the aliquots actually analyzed was recovered with an accuracy of ±10 per cent, but that a somewhat larger quantity can be determined within ±2 per cent. It is accordingly desirable to select aliquots with attention to this point.

Table VIII gives a comparison of starch determined by the colorimetric method with values determined by the reducing power of the starch after isolation as described and subsequent hydrolysis with acid. The discrepancy between the two methods is especially high for tissues of low starch content and suggests that substances other than starch which yield sugar

TABLE VI. DUPLICABILITY OF COLORIMETRIC DETERMINATION OF STARCH IN PLANT TISSUE

Tissue Analyzed	Starch in CaCl ₂ Extract	Starch in HCl Extract
	%	%
Tomato stem	10.90	10.90
	10.80	10.80
Rhubarb rhizome	32.00	32.94
	32.50	33.20
Rhubarb leaf	...	0.35
	...	0.38
Tobacco leaf E	1.50	1.38
	1.44	1.44
Tobacco leaf F	...	0.67
	...	0.63
Tobacco leaf B	...	5.50
	...	5.35
Tobacco leaf D	...	6.00
	...	5.85
Tobacco leaf J	...	6.15
	...	1.42
Tobacco stem K	...	1.38
	...	4.60
Beet root	...	4.70
	...	4.75
Alfalfa stem	...	0.16
	...	0.15
		7.45
		7.50

TABLE VII. RECOVERY OF STARCH ADDED TO STARCH-FREE BEET LEAF TISSUE

(0.200-gram samples of tissue)			
Starch Added	Starch in Aliquot Used	Starch Found	Recovery
Mg.	Mg.	Mg.	%
9.40	1.88	9.70	103
		9.60	102
		9.50	101
		9.35	99.6
		9.30	99
1.00	0.20	1.00	100
		1.05	105
		1.07	107
		0.90	90

on hydrolysis are precipitated. That this is the case was demonstrated by further extraction of the tissues after the starch had been removed and by extraction of starch-free tissues. In all cases, substances which gave reduction values and actual fermentable sugar were so obtained. Clearly, therefore, the high sugar titration values are due to contamination of the extracts with hydrolyzable substances other than starch.

The sugar titration values of the calcium chloride extracts agree in range with the hydrochloric acid extracts, provided the precipitation of the starch iodide is made at pH 1. Precipitation at pH 3 leads to higher values, and Table IX gives actual data that illustrate the magnitude of the discrepancies that may occur. The beet and rhubarb tissues were all low in true starch, but the extracts gave unusually large precipitates with iodine at pH 3, which in turn yielded much sugar on hydrolysis. Much less of this material was usually obtained at pH 1 in the cold.

It is clearly impossible to interpret the sugar titration values of the substances precipitated by iodine as being entirely due to starch. The colorimetric values, however, are identical regardless of the method of extraction or precipitation.

LOWER LIMIT OF ACCURACY OF THE METHOD. Extracts of starch from plant tissue prepared by either method frequently contain other substances that are either precipitated by iodine or adsorbed on the starch precipitate. These substances may give rise to a turbidity in the solution of free starch later obtained that interferes with the reading of the spectrophotometer. The amount of these extraneous substances varies with the tissue analyzed, but, in all cases the authors have encountered, can be minimized by heating the solution to 100° C. after the addition of the iodine reagent to the extract previously acidified to approximately pH 1.

In order to obtain an idea of the magnitude of the interference that may occur, analyses of starch-free beet leaf tissue were carried out. The extracts from this tissue gave no blue color with iodine, but yielded a small white flocculent precipitate under the conditions of the analysis. If the precipitation was made in acetic acid solution at pH 3, this precipitate was much larger and yielded a solution in water that showed a marked Tyndall effect in the spectrophotometer. On the other hand, if the precipitation was carried out at 100° C. at pH 1, the precipitate was very small and yielded a solution that was apparently clear. When diluted to 20 ml. and observed in a 3-cm. cell in the spectrophotometer, extinction coefficients of 0.032 and 0.010 were obtained, respectively. Both readings are beyond the lower limit of accuracy of the starch calibration curve of the instrument and therefore have little significance. Nevertheless the results illustrate the superiority of the iodine precipitation at pH 1, and also serve as a blank on the method when applied to the analysis of tissues very low in starch. The value 0.01 for the extinction coefficient has been repeatedly found for tissues that gave no qualitative evidence of the presence of starch. Consequently when attempts are made to estimate quantities of 0.1 mg. or less of starch, it would seem advisable to deduct 0.01 from the extinction coefficient observed to allow for this blank.

The calibration curve is constructed on the basis of 0.200 gram of tissue, the extract from which is made to 50 ml., and of this 10 ml. at most are subsequently diluted to 20 ml. The limit of the calibration is 0.1 mg. of starch; consequently the lower limit of the method is a starch concentration of 0.25 per cent of the prepared tissue. If it is desired to determine smaller proportions, a larger sample of tissue must be employed. As much as 0.5 gram can be satisfactorily extracted by the technic described.

Tissues that contain high proportions of starch are most conveniently dealt with by reducing the size of sample se-

TABLE VIII. COMPARISON OF COLORIMETRIC METHOD FOR STARCH WITH SUGAR TITRATION VALUES

	Colorimetric Starch in Tissues %	Sugar Titration Values	
		CaCl ₂ extract %	HCl extract precipitation at pH 3 %
Alfalfa stem 39	7.50	...	9.14
Alfalfa stem 40	5.85	6.54	...
Tomato stem C	9.50	10.50	...
Tomato stem B	10.60	11.70	12.54
Tomato stem A	10.90	12.34	13.02
Tomato stem residues ^a	0.48	...	0.92
	0.18	...	0.39
	0.20	...	0.40
	0.25	...	0.55
Beet root	0.15	0.37	1.77
Beet top	0.05	0.21	0.89
Rhubarb leaf	0.41	0.82	2.20
Tobacco leaf E	1.41	1.48	2.18
Tobacco leaf B	5.50
Tobacco leaf F	0.63
Tobacco stem H	0.78	...	1.13
Tobacco stem I	1.68	1.80	2.37
Tobacco stem J	1.88	...	2.23
Tobacco stem K	4.63	5.00	5.19
Rhubarb rhizome	31.88	40.02	43.00

^a Tissue first extracted by refluxing with CaCl₂ + MgCO₃ for 2 hours. Residue washed and then extracted in usual way with HCl.

TABLE IX. COMPARISON OF COLORIMETRIC METHOD AND SUGAR TITRATION UNDER DIFFERENT CONDITIONS

Tissue Analyzed	Colorimetric Starch %	Sugar Titration Values	
		CaCl ₂ extract %	HCl extract precipitation at pH 3 %
Alfalfa leaf	7.45	...	9.14
Beet top	0.00	0.18	0.89
Beet root	0.16	0.37	1.77
Rhubarb leaf	0.35	0.82	2.20
Tobacco leaf B	5.50
Tobacco leaf F	0.63
Tobacco stem K	4.70	...	5.19

lected. For tissues with 30 per cent or more, it is advisable to employ 0.100 gram or even less.

Action of Takadiastase on Starch Extracts

The purity of the starch extracts from plant tissues can be readily tested by observations of the effect of takadiastase upon them.

An aliquot of the extract that contains less than 3 mg. of starch is neutralized with sodium hydroxide and acidified with a slight excess of acetic acid; 0.5 ml. of calcium chloride and 2 ml. of a 0.1 per cent solution of takadiastase (takadiastase undiluted 900 per cent, Parke, Davis and Co.) in water are added. The solution is warmed at 50° to 52° C. for 30 minutes with occasional stirring, is cooled and acidified with 2 ml. of dilute hydrochloric acid, and a few drops of iodine-potassium iodide reagent are added. If the precipitate produced is blue, the analytical procedure may be completed as already described. If no blue precipitate is formed, it is obvious that the extract contained no substance other than starch that reacts with iodine to give a blue color.

A careful investigation of the authors' standard preparations of potato starch showed them to be free from such contaminants; this confirms the statements of Ling and Nanji (7). In addition, tests on a number of preparations of leaf tissue revealed no case in which the amount of blue precipitate obtained after digestion of the extract with takadiastase gave readings at the spectrophotometer that could be regarded as significant.

Discussion

The colorimetric method employs three distinct steps, each of which contributes markedly to the specificity for starch. The preliminary dilute alcohol extraction of the tissue removes compounds such as glucosides and alkaloids, some of which yield insoluble colored compounds with iodine (1, 2). The precipitation of the starch with iodine eliminates a large group of polysaccharides which may be present in the starch extract but which are not precipitated by iodine. The utilization of the highly specific blue color of the iodine-starch complex for the quantitative measurement eliminates unknown carbohydrate compounds which may have been precipitated by the iodine or adsorbed on the starch precipitate. When formed in the presence of a large definite excess of iodine, this color is reproducible and stable. In addition, the use of the light filter which transmits a band of light of wave

length most strongly absorbed by the iodine-starch complex further contributes to the over-all specificity of the method.

The only source of interference that may be anticipated is from substances of the amylohemiacellulose type described by Schulze (13), Schryver and Thomas (12), and Ling and Nanji (7), which occur in certain starch-bearing seeds, in fruits, leaves, and stem tissues. These substances give an intense blue, or blue-violet, color with iodine, but differ from true starch in that they are not digested by takadiastase.

The present method of determining starch is essentially a comparison between starch isolated from the tissue under analysis and potato starch taken as standard. The authors have found no evidence of the presence of amylohemiacellulose in the standard starch they have used, nor in the tissues they have employed in their tests of the method. Obviously, however, tests should be made for such compounds before applying the colorimetric method in new cases. On the other hand, however, such information as is available in the literature indicates that the relative proportion of these compounds is usually very small, so that serious errors will seldom be encountered.

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Determination of Zinc in Soils

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MANY methods for the determination of small amounts of zinc in various materials have appeared in recent years. A review of those appearing prior to 1932 is given by Todd and Elvehjem (15). Since that time methods for the determination of zinc have been reported by Hibbard (7) and others (10, 12). Most of these are unsatisfactory for soil probably because of the large amounts and number of interfering substances present in them. Procedures involving the precipitation of iron and aluminum from the solution before the zinc is precipitated (1, 13) seem to be unsatisfactory because these bulky precipitates retain zinc, and it is difficult to remove all the iron.

In the work reported in this paper on the determination of zinc in soils, variations of several methods are used, including a modification of Hibbard's method for the determination of zinc in plant material in which the zinc is precipitated by

hydrogen sulfide from a properly buffered solution, after a preliminary precipitation with hydrogen sulfide to remove certain impurities. An acid concentration higher than that recommended by Hibbard was found necessary, probably because of the large mass of soluble salts resulting from a soil fusion. The zinc is determined with Nessler tubes by a method adapted to amounts found in soils.

Turbidimetric Determination of Zinc

Several methods (3, 6, 11, 16) have been used in the determination of small amounts of zinc, such as ferrocyanide turbidity, ferrocyanide titration, iodometric titration, polarigraph, and indirectly a colorimetric phosphate method. The ferrocyanide turbidity method has been used by the greatest number of investigators and was adopted for this work.

That the degree of opalescence produced by zinc in a potassium ferrocyanide solution is dependent on time, salt con-

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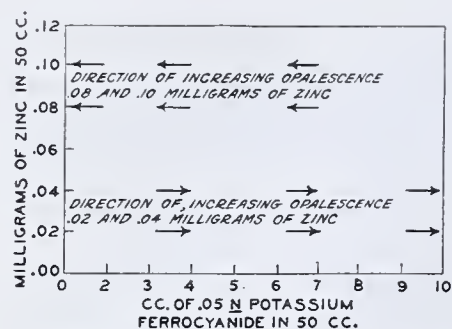


FIGURE 1. CHANGE IN OPALESCENCE WITH VARIOUS AMOUNTS OF POTASSIUM FERROCYANIDE AND ZINC

amounts of zinc from 0.02 to 0.1 mg. in 50 cc. of solution is given in this paper.

The potassium ferrocyanide used by the various workers varied from 0.1738 to 0.00264 gram per 50 cc. A comparison of opalescence was made using from 0.02 to 0.1 mg. of zinc and from 1 to 10 cc. of 0.05 *N* potassium ferrocyanide in 50 cc. Fifteen cubic centimeters of *N* hydrochloric acid were used in all these tests. The readings of the various amounts of zinc and potassium ferrocyanide are depicted on a parallelogram shown in Figure 1.

For each amount of zinc the opalescence varied with each amount of potassium ferrocyanide. With 0.10 and 0.08 mg. of zinc, opalescence was greatest with 1 cc. of the 0.05 *N* potassium ferrocyanide and least with 10 cc. With 0.02 and 0.04 mg. of zinc, the opalescence produced was reverse order, being greatest with 10 cc. of the 0.05 *N* potassium ferrocyanide and practically none with 1 cc. With amounts of zinc from 0.02 to 0.1 mg. and 15 cc. of *N* hydrochloric acid in 50 cc. it would seem about 5 cc. of 0.05 *N* potassium ferrocyanide should be used.

The effects of acid on the opalescence of zinc in amounts from 0.02 to 0.1 mg. in potassium ferrocyanide solution are shown in Figures 2 and 3.

The readings from which Figures 2 and 3 were made are approximate, because the same amount and shade of opalescence are reproduced only by identical conditions in all respects. Three milligrams of zinc with 3 cc. of *N* hydrochloric acid were taken as a standard for the readings in both figures. Figure 2 shows that with 0.02, 0.03, and 0.04 mg. of zinc there is opalescence with 3 cc. of *N* hydrochloric acid. The opalescence increases up to 9 cc. with 0.02 and 0.03 mg. and up to 12 cc. with 0.04 mg. of *N* hydrochloric acid and zinc, respectively. After maximum opalescence is reached the opalescence decreases with increasing amounts of acid until between 18 and 24 cc. of *N* hydrochloric acid there is no opalescence.

Figure 3 shows the apparent amounts of zinc as judged by opalescence produced with 3, 9, 12, and 15 cc. of *N* hydrochloric acid on from 0.03 to 0.12 mg. of zinc. Three cubic centimeters of *N* hydrochloric acid show the least opalescence for the various amounts of zinc and the least difference between the various amounts of zinc. Fifteen cubic centimeters of *N* hydrochloric acid have the greatest opalescence and the greatest differences between the various amounts of

concentration, kind of acid, strength of acid, and the potassium ferrocyanide-zinc ratio has been pointed out by several investigators (2, 5, 14). The degree of dependence of opalescence on the potassium ferrocyanide-zinc ratio and amount of hydrochloric acid for

zinc. Figure 2 has shown a disappearance of opalescence with more than 15 cc. of *N* hydrochloric acid with very small amounts of zinc. From these results it would seem that 15 cc. of *N* hydrochloric acid are about right to use in 50 cc. of solution with zinc ranging from 0.03 to 0.1 mg.

The zinc as separated was free of contaminating salts except for the small amount of sulfide in combination with the zinc. Several investigators add salts of various kinds to increase the opalescence. Added salts were found to impart a greenish tinge to the opalescence and seemed to hasten its breaking down, and for that reason are not used in this method. The clearest opalescence was secured by using acid alone. Maximum opalescence is attained in about 3 minutes and persists for 15.

Analytical Procedure

The soil sample is first fused with potassium pyrosulfate and the fusion disintegrated in a hot dilute hydrochloric acid solution (13). The silica is removed by filtration and the filtrate and washing are evaporated to a fairly small volume. The acidity of this solution is fixed at 0.4 *N* and the interfering members of the first hydrogen sulfide group in qualitative analysis are removed with hydrogen sulfide. The solution is buffered, a filter aid added, and the pH fixed at about 3.5 (neutral gray color to bromophenol blue or bromochlorophenol blue). The zinc is then precipitated with hydrogen sulfide and filtered. After thorough washing it is dissolved off the paper with 1 *N* hydrochloric acid. The acid solution containing the zinc is made up to a definite volume and the zinc determined with Nessler tubes on an aliquot by the ferrocyanide method.

REAGENTS AND PRECAUTIONS. Only iron, nickel, or monel metal screens and grinding equipment should be used in the preparation of the sample, avoiding all brass. Zinc-free glassware must be used. Pyrex ware is satisfactory.

The buffer solution (9) for zinc precipitation consists of 650 grams of ammonium sulfate, 500 grams of citric acid, 200 cc. of 90 per cent formic acid, and 500 cc. of concentrated ammonium hydroxide in 2.5 liters. The 3.2 pH buffer solution consists of 37 cc. of 0.1 *N* hydrochloric acid and 2.5508 grams of potassium acid phthalate in 250 cc. of solution (4). The indicator solution is prepared by dissolving 1 gram of bromochlorophenol blue or bromophenol blue in 28.5 cc. of 0.1 *N* hydroxide and diluting to 2.5 liters with water.

FUSION. Two 5-gram portions of soil are fused in 50-cc. platinum crucibles, each with 12 to 20 grams of potassium pyrosulfate (8). If the soil is mixed with half or less of pyrosulfate and the remainder added in one or more portions as the fusion progresses, boiling over will be practically prevented. The amount of potassium pyrosulfate needed is largely determined by the quan-

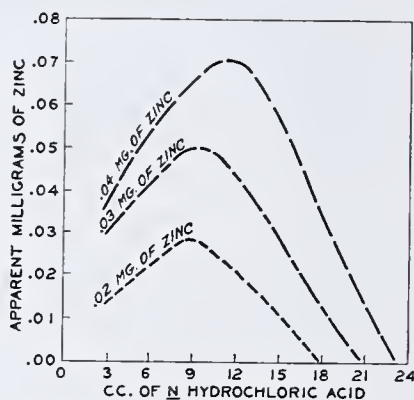


FIGURE 2. EFFECT OF AMOUNT OF HYDROCHLORIC ACID ON OPALESCENCE OF SMALL AMOUNTS OF ZINC

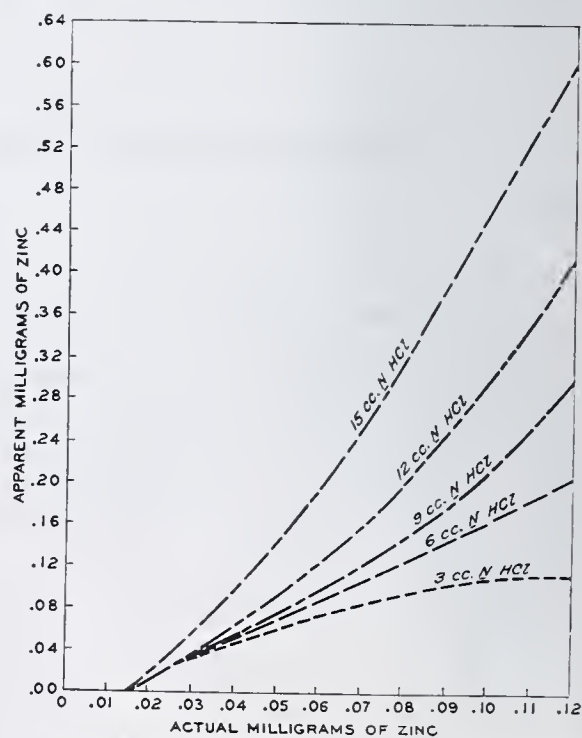


FIGURE 3. EFFECT OF AMOUNT OF HYDROCHLORIC ACID ON OPALESCENCE OF ZINC IN POTASSIUM FERROCYANIDE SOLUTION

tity of calcium and organic matter in the sample, more being required as these components increase. The fusions can usually be made almost completely with the lid off, covering only toward the end.

SEPARATION OF IMPURITIES. The fusions are cooled and placed one at a time in a 400-cc. beaker containing 250 cc. of water and 10 cc. of hydrochloric acid. After they have loosened and the crucibles and lids have been removed and washed, the solution is evaporated to about 100 cc. on a hot plate. If much calcium is present, the solution must be kept heated almost to the point where bumping will occur in order to disintegrate the fusion. If the fusion is allowed to cool gradually before being placed in the acid solution for disintegration, it will come free from the crucible much more readily than if the fusion is placed in the solution hot or its cooling hurried unduly. The solution is filtered on a Büchner funnel, removing the silica and a good part of the gypsum. The precipitate is washed several times with cold distilled water. The filtrate and washings are evaporated to 100 to 150 cc.

The acidity of the solution is now fixed at 0.4 *N* by adding the proper amount of 5 *N* sodium hydroxide. This is determined by titrating 1 cc. of the unknown solution in a 100-cc. beaker, with 1 cc. of bromophenol blue indicator solution to the same color as an identical volume of pH 3.2 buffer solution with 1 cc. of bromophenol blue indicator. It is convenient to have ready for comparison 100-cc. beakers containing, respectively, 10, 15, and 20 cc. of the buffer solution with 1 cc. of the indicator solution. From this result and the volume of solution the amount of 5 *N* sodium hydroxide required to bring the solution to 0.4 *N* acidity can be calculated.

After the normality is fixed, hydrogen sulfide is passed rapidly into the cold solution (10) for 15 minutes, the solution is filtered, and the precipitate washed with a 0.4 *N* hydrochloric acid solution, saturated with hydrogen sulfide. The precipitate is discarded.

SEPARATION OF ZINC. To the filtrate, approximately 250 cc., are added 25 cc. of buffer solution and 2.5 cc. of bromophenol blue indicator solution. The solution is titrated to a gray color, or slightly beyond, with 5 *N* sodium hydroxide. One cubic centimeter of 5 per cent talc suspension is then added and the zinc precipitated by passing a rapid stream of hydrogen sulfide for 30 minutes.

The precipitate is filtered and the filter carefully washed with hydrogen sulfide water containing 4 cc. of 90 per cent formic acid per liter. This washing frees the filter of iron. At least four washings are necessary and finally the precipitate and tips of the funnels are washed once with distilled water. The zinc sulfide on the paper is then dissolved by washing the filter with 30 cc. of 1 *N* hydrochloric acid into a 100-cc. volumetric flask and made to volume by washing the paper repeatedly with distilled water.

DETERMINATION OF ZINC. Aliquots of 10 to 25 cc. of the solution from separation of the zinc are placed in 50-cc. Nessler tubes. The acidity is increased until each one has 15 cc. of *N* hydrochloric acid, water is added to make 45 cc., and finally 5 cc. of the 0.05 *N* potassium ferrocyanide are added. The whole is mixed thoroughly and then compared with a set of standards made up in a similar manner. If talc filter acid and water are saturated with hydrogen sulfide and filtered, and the hydrochloric acid used afterward for the standards is run through this filter, the standards will have the same shade of color as the unknowns, a considerable aid in quick reaching of the unknowns. Comparison of unknowns with standards is best made by placing the Nessler tubes over fine print as suggested by Birekner (2).

Application and Results

The method was checked by adding 1 mg. of zinc to an acid and a neutral soil at various steps in the process, and the added zinc recovered. The results are shown in Table I.

TABLE I. RECOVERY OF ADDED ZINC FROM AN ACID AND NEUTRAL SOIL			
Stage in Method When Zinc Was Added	Zinc Added Mg.	Inherent Zinc in Soil Sample Mg.	Total Zinc Recovered Mg.
Monroe silt loam, virgin soil, 3 to 6 inches, pH 4.68			
Zinc applied in solution before fusion	1.00	0.40	1.40
	1.00	0.40	1.40
Zinc added dry before fusion	1.00	0.40	1.40
	1.00	0.40	1.40
Zinc added in solution before fusion	1.00	0.40	1.40
Fused very hard	1.00	0.40	1.40
Yaholla fine sandy loam, 24 to 36 inches, pH 7.00			
Zinc added before silica filtered	1.00	0.22	1.20+
	1.00	0.22	1.20+
Zinc added after silica filtered	1.00	0.22	1.20+
	1.00	0.22	1.20+

The zinc content of six soils ranging in reaction from pH 4.25 to 8.40 as determined by this method is given in Table II. This table shows considerable variation in the zinc content of soil profiles. The lowest amount of zinc in any horizon is 0.04 mg. per 10-gram sample and the highest amount is 0.83 mg. Rosette of pecans has been found to be associated with deficiencies of available zinc in soils and a discussion of this relationship will be presented in another publication.

TABLE II. ZINC CONTENT OF TYPICAL SOILS

(Amount per 10 grams)						
	Yaholla Fine Sandy Loam	Uvalde Silty Clay Loam	Frio Silty Clay Loam	Acadia Very Fine Sandy Loam	Catalpa Silty Clay Loam	Ochlockonee Fine Sandy Loam
Depths Inches	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
0-3	0.73	0.23
3-6	0.83	0.25
6-12	0.63	0.53	0.53	0.04
Feet	0.63	0.38	0.53	0.09	0.73	0.25
1-2	0.53	0.38	0.53	0.17	0.83	0.23
2-3	0.43	0.43	0.63	0.21	0.83	0.33
3-4	0.43	0.38	0.63	0.19	0.83	0.38
4-5	0.43	0.33	0.63	0.29	0.83	0.33
5-6	0.43	0.43	0.63	0.31	0.83	0.33
6-7	0.43
7-8	0.53
8-9	0.63
9-10	0.68
10-11	0.73
11-12	0.78

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Recovering Chloroform from Used Dithizone Solutions

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CHLOROFORM from used dithizone solutions can be economically recovered by first removing any aqueous layer, then washing until colorless with commercial sulfuric acid equal to 5 or 10 per cent of its volume, treating with lime, distilling in the presence of some of the excess lime, and finally adding alcohol (1.0 to 1.5 per cent by volume). The sulfuric acid removes the organic impurities, while the lime neutralizes the excess acid or any acid resulting from the decomposition of the chloroform during distillation, and the alcohol acts as a preservative. The product meets the tests of the U. S. Pharmacopeia and is suitable for further use with dithizone or in other procedures.

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Measuring the Susceptibility of Asphalts to Temperature Changes

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PRIOR to the introduction of modern distillation methods into the petroleum industry, the sources of petroleum asphalts were comparatively few. Subsequently, however, the increased use of vacuum pipe stills, as well as other improvements in refining methods, opened a considerably broader field, resulting in the production of asphalts from sources which previously could not be processed for that purpose in existing equipment without some decomposition. Modern methods have also made possible the manufacture of a larger number of asphalt grades than were formerly produced.

Asphalts, in general, are classified in several groups according to their use as binders and paving asphalts for the construction of roads, saturants and roofing asphalts for the roofing trade, as well as innumerable specialty products for many other uses. Each classification is subdivided into numerous grades depending upon their consistency, which is usually designated by one or more of the standardized tests, such as softening point, penetration, and viscosity. The ring and ball softening point is defined as that temperature at which a sample of asphalt, molded in a ring of standard size and upon which a 0.94-cm. (0.375-inch) steel ball has been set, sags under the weight of the ball to a depth of 2.5 cm. (1 inch) when suspended in a fluid, either water or glycerol, heated at a definite rate of 5° C. (9° F.) per minute. The penetration is defined as the depth, measured in one-hundredths of a centimeter, to which a standard-size needle penetrates the asphalt under definite conditions of temperature, weight, and time. Because of the nature of asphalts, these methods are necessarily fixed, arbitrary, and closely defined, in order that comparable results may be obtained. The viscosity may be determined in numerous ways by means of efflux-type or torsion-type viscometers.

While these tests *per se* serve to define the physical characteristics of an asphalt under specified conditions, they do not, individually or collectively, give a clear picture as to the behavior over the wider range of conditions encountered in actual service.

Recently, there has been an increasing demand from the asphalt consumer for some simple method by which the behavior of an asphalt under service conditions can be definitely

The need for some suitable means of expressing the change in consistency of asphalts over the wide range of temperature usually encountered in actual service is demonstrated. While no single factor has been developed which will adequately serve to measure the temperature susceptibility over the entire desired range of conditions, three methods are suggested which can be used in conjunction with one another for this purpose. The softening point-penetration index indicates the susceptibility over a narrow range of normal atmospheric temperatures, the ratio of the penetration at 25° C. (77° F.) to the penetration at 0° C. (32° F.) at subnormal, and the fluidity index at elevated temperatures.

indicate numerically the consistency changes of an asphalt at normal, subnormal, and elevated temperatures. It should be borne in mind, however, that asphalts have other characteristics just as important which do not come within the scope of this paper.

Review of Some Present Methods

In dealing with asphalts, the term "susceptibility" is generally employed to indicate the tendency of this material to change in consistency with changes in temperature. A product that changes consistency rapidly with temperature is spoken of as possessing a high susceptibility, and one which changes slowly with temperature has a low susceptibility.

If an asphalt which is highly susceptible is used as a filler in block pavements, either wood or stone, the heat under normal summer conditions will cause the asphalt to soften almost to the point of being fluid. This will ooze out of the joint onto the blocks, rendering them sticky. An asphalt with low susceptibility will not soften to any such degree under the same conditions and although expansion will take place, the bitumen will remain in a more or less solid, nonsticky condition. In an asphalt macadam road, other conditions being equal, a highly susceptible asphalt tends to lower road stability and cause displacement under the action of heavy traffic in hot weather, because the asphalt will soften to a greater degree and hence lose more of its bonding power than one of low susceptibility. On the other hand, it is sometimes desirable to have an asphalt which becomes fluid rapidly as the temperature is raised. In the manufacture of some impregnated products a highly susceptible asphalt, in this case one which becomes fluid more rapidly at elevated temperatures than one of low susceptibility, tends to impregnate the material to a greater extent than the less susceptible bitumen, under the same conditions.

Thus, susceptibility of an asphalt is a property which manifests itself readily and is easily recognizable in all fields where asphalt is employed. The existing methods of measuring this property are not entirely suitable, either because of the limited range of consistencies over which they may be calculated or because they require the use of special apparatus and methods of testing not readily available nor widely in use.

SUSCEPTIBILITY FACTOR. Two methods of expressing the susceptibility factor which have been used for a number of years are calculated from the following formulas:

$$\text{Susceptibility factor} = \frac{\text{penetration at } 46.1^{\circ} \text{ C. per 50 grams per 5 seconds} - \text{penetration at } 0^{\circ} \text{ C. per 200 grams per 60 seconds}}{\text{penetration at } 25^{\circ} \text{ C. per 100 grams per 5 seconds}} \quad (1)$$

$$\text{Susceptibility factor} = \frac{\text{penetration at } 37.8^{\circ} \text{ C. per 100 grams per 5 seconds}}{\text{penetration at } 25^{\circ} \text{ C. per 100 grams per 5 seconds}} \quad (2)$$

measured. In an attempt to meet one phase of this condition, the available asphalt data obtained from various crude sources were reviewed with the result that factors were evolved which

Method 1 has gradually been almost entirely supplanted by method 2, which was originally given in the paving asphalt specifications for one of our large cities. Application of the

data to these two methods indicates that, while they give results in the same order of magnitude, they are not always in agreement. It was also observed that no calculations could be made on asphalts softer than 70 to 75 penetration at 25° C. (77° F.) because the values of penetration at 37.8° C. (100° F.) and 46.1° C. (115° F.) were indeterminate, owing to the limitations of the penetration test. The limit of penetration is approximately 350, corresponding to the depth of the asphalt container specified by the test. For a given source of asphalt, the factors varied over a rather wide range, depending upon the consistency.

A third type of factor has been suggested by Abraham (1).

$$\text{Susceptibility factor} = \frac{\text{hardness at } 0^\circ \text{ C.} - \text{hardness at } 46.1^\circ \text{ C.}}{\text{softening point (Kramer-Sarnow) } ^\circ \text{ C.}} \quad (3)$$

Since the hardness, defined as the cube root of the number of grams which must be applied to a circular flat surface 1 sq. cm. in area to cause it to displace the substance at a speed of 1 cm. per minute, is determined by a special apparatus not in general use, this method has little practical value. The Kramer-Sarnow softening point differs from the more common ring and ball method in that the former is obtained by placing 5 grams of mercury on a plug of asphalt formed in a glass tube of definite size. The Kramer-Sarnow softening point is the temperature at which the mercury drops through the tube.

The Kramer-Sarnow softening point is usually 8° to 14° C. lower than the ring and ball softening point.

FLUIDITY FACTOR. The correlation of the viscosity of an asphalt and its penetration forms the basis for the calculation of a "fluidity factor" (4) which is used in some sections of the country for describing the change in consistency of an asphalt with temperature. The formula in this case becomes:

$$\text{Fluidity factor} = \left(\frac{\text{Furol viscosity at } 135^\circ \text{ C.} - \text{penetration at } 25^\circ \text{ C. per 100 grams per 5 seconds}}{\text{penetration at } 25^\circ \text{ C. per 100 grams per 5 seconds}} \right) \quad (4)$$

As pointed out by Zapata (4), this factor is of particular value over the range of paving grades, although it does not remain constant for asphalts from a given source but varies with the consistency. An asphalt of 122 penetration at 25° C. per 100 grams per 5 seconds and Furol viscosity at 135° C. (275° F.) of 222 seconds shows a factor of 122 by this method, whereas a product from the same source of 29 penetration at 25° C. (77° F.) and 799 Furol viscosity at 135° C. (275° F.) shows a value of 223.

FLOAT TEST INDEX. Another method known as the float test index, which has been used in one of the midwestern state specifications for paving asphalts, is calculated as follows:

$$\text{Float test index} = \sqrt{F \times P} \quad (5)$$

where F is the float test in seconds at 80° C. (176° F.) and P the penetration at 25° C. per 100 grams per 5 seconds.

The float test is a consistency test in which asphalt is poured into a standardized mold or collar. After cooling the sample for the designated time, the collar is screwed into the bottom of the aluminum float or saucer and the assembly floated in a water bath at the desired temperature. As the plug of asphalt is warmed by the water, it becomes fluid and is forced upward and out of the collar. The time in seconds between placing the apparatus on the water and when the water breaks through the material, causing the float to sink, is taken as the float test of the material.

The lack of specific data on the float test at 80° C. (176° F.) precludes a detailed discussion on this factor, although it would appear that this method would be more or less limited to those asphalts in the paving range of consistencies—i. e., from 30 to 95 penetration at 25° C. (77° F.).

HOEPFNER-METZGER VISCOSITY LAW. The Hoepfner-Metzger viscosity law of normal tars and asphalts (3) has also been suggested as a means of determining the susceptibility of asphalts. The so-called Hoepfner-Metzger "rigid point" of asphalts and Ubbelohde drop-point form the basis of this system. Any tests which measure the viscosity of an asphalt can be correlated by means of this law. As in the case of some other factors, it requires tests employing special apparatus and methods not in general use in this country, thus limiting the wide application of such a system.

Evolution of Suggested Methods

Before discussing the new methods evolved, a few comments should be made on the familiar viscosity index system for evaluating lubricating oils as developed by Dean and Davis (2), since two of the proposed factors may be described as being essentially indexes similar to this system. Briefly, the Dean and Davis system consists in obtaining the Saybolt Universal viscosities of two series of oils, each derived from an extreme type of crude, at the standard temperatures of 37.8° C. (100° F.) and 98.9° C. (210° F.). From these basic figures, a general relationship between the viscosity at 37.8° C. (100° F.) and at 98.9° C. (210° F.) was formulated for each series. From these equations a system of so-called viscosity indexes was developed which indicates the viscosity-temperature coefficients of any oil on a scale in which the series of oils (Texas-Coastal) having a high temperature coefficient are designated as 0 and those with a low coefficient (Pennsylvania) as 100.

The usefulness and widespread adoption of this method for evaluating the viscosity-temperature characteristics or susceptibility, as it might be called, of lubricating oils is general knowledge.

We are interested at present in one of the important characteristics of asphalts—namely, the degree of hardening or softening which takes place, or in other words, the susceptibility over the temperature range more or less governed by climatic conditions. At these temperatures, asphalts of particular interest are those with measurable penetrations. These considerations would suggest that a factor used for indicating susceptibility should include both the softening point and penetration at 25° C. (77° F.).

The statement should probably be made at this point that no single factor or method has been developed in the present investigation, which will adequately serve to measure the susceptibility over the entire desired range of consistency and temperature. Three methods will be described, however, which can be used in conjunction with one another to give a fairly complete picture of the susceptibility characteristics of an asphalt.

SOFTENING POINT-PENETRATION INDEX. From the correlation of data from a large number of crude sources, a general relationship has been found to exist between the softening point and penetration for straight reduced asphalts—i. e., those produced by steam and/or vacuum distillation, from any given source. This relationship, which gives a straight line on log-log coordinate paper, may be expressed by the equation:

$$\log M = a \log P + \log k \quad (6)$$

$$\text{or} \quad M = kP^a \quad (7)$$

where M is the ring and ball softening point, in ° F., P the penetration, and a and k are constants depending upon the source of the asphalt and the temperatures at which the penetration is taken. While this relationship gives no indication, by itself, of the change in consistency of any one asphalt with

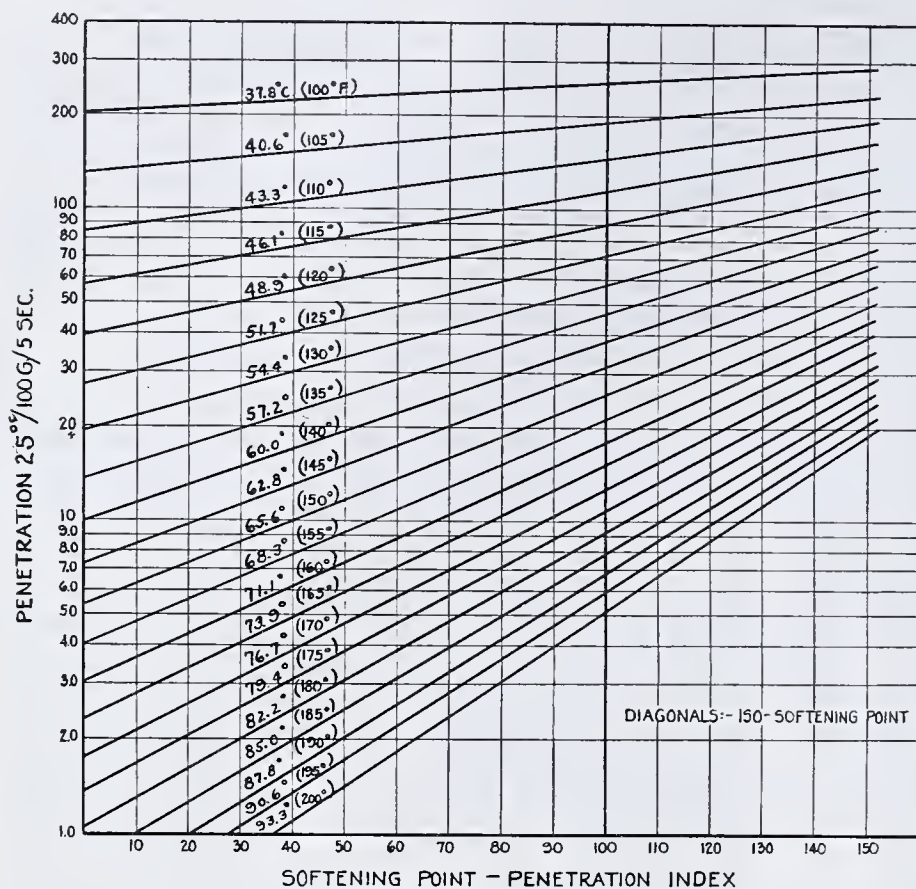


FIGURE 1

temperature, experience has shown in a general way that the higher the penetration of an asphalt at 25° C. (77° F.) for a given softening point, the less susceptible is that asphalt to temperature changes.

An attempt to express this general relationship numerically resulted in the development of the so-called softening point-penetration index. From the data obtained on two series of asphalts from sources of extreme types, a chart (Figure 1) was constructed. Basic figures used for developing the arbitrary scales were obtained from accurate tests on vacuum-pipe still reduced asphalts from Heavy Mexican and petroleum tar. Asphalts from Heavy Mexican crude were arbitrarily chosen as 100 on the index scale as representing products having a low consistency-temperature coefficient, while those from petroleum tar were selected as the other extreme—that is, as 0 on the scale, representing asphalts with a high consistency-temperature coefficient. These two extremes correspond to the use of Pennsylvania and Texas-Coastal oils, respectively, as extremes in the Dean and Davis lubricating oil viscosity index system. In this discussion, petroleum tar is to be considered as the residue from the cracking of virgin gas oil under high temperature and pressure. As in the viscosity index system, the sources of asphalts selected as standards do not represent either the lowest or highest known susceptibilities.

In Figure 1, the ordinate represents the penetration at 25° C. per 100 grams per 5 seconds, those for Mexican asphalt being on the right and for petroleum tar products on the left of the 0 to 100 scale. The abscissa represents the index number, which may be extended above 100 or below 0, and the diagonal lines indicate constant or iso-softening point. Thus, for example, the straight line shown for 54.4° C. (130° F.) softening point was drawn between 19.5 penetration at 25° C. (77° F.) at 0 index, the penetration of a petroleum tar asphalt of this softening point, and 57 penetration at 25° C. (77° F.), the corresponding value at 100 index for Mexican asphalt. As an example of the use of this chart, it is desired to determine the softening point-penetration index of an asphalt having a softening point of 54.4° C. (130° F.) and 40 penetration at 25° C. per 100 grams per 5 seconds. The penetration is read from the ordinate scale on the left, followed horizontally to the right until it intersects the 54.4° C. (130° F.)

iso-softening point line. At this point, the index number is read vertically downward from the abscissa scale giving a value of 67.

This index may be applied to oxidized asphalts as well as straight reduced grades. The former are made by air-blowing or refining a straight reduced crude residuum usually of soft consistency which is commonly referred to as the base. It is known that the greater the extent of oxidation, the lower is the susceptibility of an asphalt. In other words, the higher the softening point of an oxidized asphalt blown from a given base, the higher is its index. Likewise, for a given softening point, the softer the consistency of the oxidizing base, the higher is the index.

Table I gives the values of this index for asphalts from various sources over the relatively narrow range of paving asphalts from 30 to 95 penetration at 25° C. (77° F.) as well as for the whole range from 0 to 200 penetration at 25° C. (77° F.).

Mexican and petroleum tar asphalts have obviously a 100 and 0 index, respectively, over the entire range since they are the assumed standards. The asphalts from the remaining sources vary somewhat, particularly over the wide range, since the softer asphalts from any given source usually display a higher index.

From the values in Table I, it appears that the softening point-penetration index affords a ready means of classifying asphalts as to their susceptibility characteristics at what the authors chose to call normal temperatures—i. e., 25° C. (77° F.).

TABLE I. NUMERICAL MAGNITUDE OF SOFTENING POINT-PENETRATION INDEX

Asphalts ^a	Range of Values for Softening Point-Penetration Index	
	Paving range, 30-90 penetration at 25° C.	Whole range, 0-200 penetration at 25° C.
Mexican	100	100
Venezuelan	85-88	78-90
Colombian	67-77	67-100
Heavy Smackover	82-94	72-110
West Texas	59-62	52-90
Heraldton	70-76	70-80
Midcontinent	59-65	52-75
Van Zandt	68-75	68-110
California (Kern River)	14-27	4-58
East Venezuelan	10-27	5-65
Petroleum tar	0	0

^a Straight reduced asphalts.

Penetration range, penetration 25° C. per 100 grams per 5 seconds.

SUSCEPTIBILITY AT SUBNORMAL TEMPERATURES. It was previously shown that methods 1 and 2 for determining the susceptibility factor of an asphalt were limited to asphalts with a maximum penetration of 70 to 75 at 25° C. (77° F.). Another method which has been used from time to time in practice and which extends the range of asphalts consists in calculating the ratio of penetration at 25° C. per 100 grams per 5 seconds and penetration at 0° C. per 200 grams per 60 seconds. Thus, at subnormal temperatures, the susceptibility becomes:

$$\text{Susceptibility factor} = \frac{\text{penetration at 25° C. per 100 grams per 5 seconds}}{\text{penetration at 0° C. per 200 grams per 60 seconds}} \quad (8)$$

This method not only extends the range over which a factor can be obtained but also indicates the behavior of an asphalt

over the temperature range from 25° to 0° C. (77° to 32° F.). The characteristics of an asphalt, as the temperature is lowered, are just as important, if not more so, than at higher temperatures because it is at the lower temperatures that asphalts fail by cracking and thus lose their protective or bonding properties. From these considerations, this method possesses distinct advantages over methods 1 and 2. The available data for various sources were calculated by method 8 and shown in Table II.

In this case, Mexican asphalts showed a fairly constant factor of 3.3, whereas the petroleum tar asphalts varied over the wide range shown. The smaller the ratio of the two penetrations, the lower is the susceptibility of the asphalt over this temperature range.

TABLE II. NUMERICAL MAGNITUDE OF THE SUSCEPTIBILITY FACTOR AT SUBNORMAL TEMPERATURES

(Susceptibility factor = $\frac{\text{penetration at 25° C. per 100 grams per 5 seconds}}{\text{penetration at 0° C. per 200 grams per 60 seconds}}$)

Asphalts ^a	Range of Susceptibility Factor Values	
	Paving range, 30-90 penetration at 25° C.	Whole range, 0-200 penetration at 25° C.
Mexican	3.3	3.3
Venezuelan	3.4-3.8	3.3-4.5
Colombian	3.5-5.0	3.3-5.5
Heavy Smackover	2.71-3.50	2.5-5.0
West Texas	4.6-5.8	4.2-9.0
Healdton	5.4-6.6	5.2-9.0
Midcontinent	3.7-4.8	3.4-7.0
Van Zandt	3.2-4.2	1.8-7.0
California (Kern River)	12.5-13.3	12.5-13.3
East Venezuelan	4.4-5.2	3.8-10.0
Petroleum tar	7.0-17.0	7.0-17.0

^a Straight reduced asphalts.
Penetration range, penetration at 25° C. per 100 grams per 5 seconds.

FLUIDITY INDEX. In order to determine the susceptibility at elevated temperatures, the so-called fluidity index was developed in essentially the same manner as the softening point-penetration index, but using the penetration at 25° C. per 100 grams per 5 seconds and Furol viscosity at 135° C. (275° F.) as the required inspections. Experience has shown that the higher the softening point-penetration relationship an asphalt possessed, the less susceptible it was to changes in temperature. To carry this one step further, it has been generally found that of two asphalts with the same penetration at 25° C. (77° F.) that product which shows the higher viscosity at a given temperature is less susceptible than the material with the lower viscosity. Hence, the penetration can be linked with viscosity to give an indication of changes in consistency at more or less elevated temperatures.

In constructing the fluidity index chart (Figure 2), the same two series of asphalts were used as in the softening point-penetration index—that is, Heavy Mexican asphalts were arbitrarily taken as 100 and petroleum tar asphalts as 0 in the index scale. The ordinate in this case represents the Furol viscosity at 135° C. (275° F.), the abscissa the fluidity index, and the diagonal lines indicate constant penetration at 25° C. (77° F.).

By applying a large number of data to this index, results such as given in Table III are obtained.

The viscosity at 135° C. (275° F.) was chosen because it was found that data could be obtained at this temperature over the important range of consistencies from 200 to 25 penetration at 25° C. (77° F.). While higher temperatures may be employed, the differences between asphalts from various

sources are not as marked and for softer asphalts the limit of accuracy of the Furol viscometer enters the picture. Similarly, at low temperatures, the viscosities on the harder asphalts are unduly high with the accompanying sacrifice of accuracy. This index can also be applied to oxidized asphalts since, for a given penetration, the rise in viscosity is dependent upon the extent of oxidation. As in the case of the softening point-penetration index, the softer the base from which an oxidized asphalt is blown, the higher will be its index.

TABLE III. NUMERICAL MAGNITUDE OF THE FLUIDITY INDEX

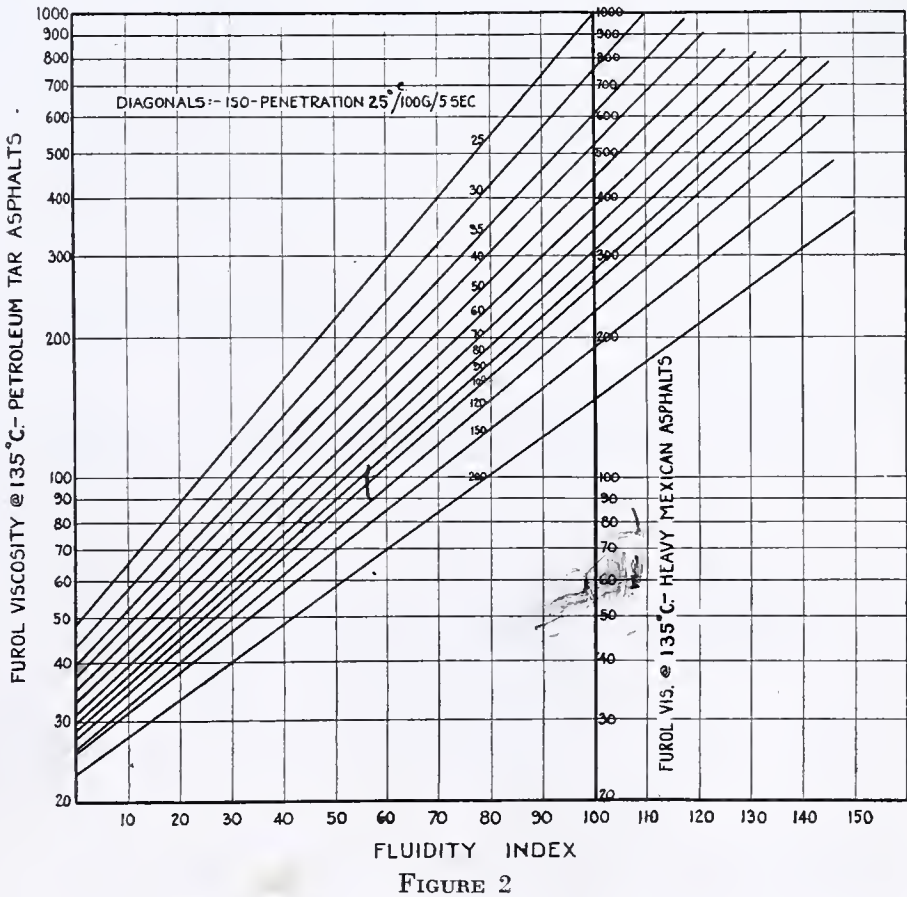
Asphalts	Range of Fluidity Index Values	
	Paving range, 30-95 penetration at 25° C.	Whole range, 0-200 penetration at 25° C.
Mexican	100	100
Venezuelan	85-87	76-87
Colombian	79-81	77-81
Midcontinent	83-86	83-86
Van Zandt	77-79	77-79
California (Kern River)	45	...
California (Kern River oxidized)	54-60	...
West Texas (straight reduced)	69-71	69-71
West Texas oxidized (41-50 penetration at 25° C.)	84	...
Petroleum tar	0	0

Discussion of Results

The present study has indicated the improbability of finding a single factor or index which will cover a wide range of consistencies and adequately serve to measure the susceptibility of an asphalt over the entire range from subnormal atmospheric temperatures to elevated temperatures. It does not necessarily follow that an asphalt which shows a high softening point-penetration index value will also display a low susceptibility factor at low temperatures and a high fluidity factor at elevated temperatures.

Table IV represents a comparison of some of the data to illustrate this feature.

For example, Colombian 53 penetration asphalt shows a lower softening point-penetration index than a 55 penetration



Healdton asphalt—i. e., 70 as compared with 73, respectively—although the subnormal temperature susceptibility for the latter is considerably higher than for the former asphalt. In other words, while the Healdton asphalt is not as susceptible at normal temperatures as the Colombian grade, the latter does not harden as rapidly as the temperature is lowered. A similar example can be shown with respect to the fluidity index. West Texas asphalt with 50 penetration at 25° C. has the same softening point-penetration index as a Midcontinent asphalt of the same consistency, although at elevated temperatures, as measured by the fluidity index, the Midcontinent asphalt has a higher index than the former. In this case also, the low temperature susceptibility is lower for the Midcontinent than for the West Texas product.

TABLE IV. CHANGES IN SUSCEPTIBILITY CHARACTERISTICS BETWEEN LOW AND ELEVATED TEMPERATURES

Source and Grade	Softening Point-Penetration Index	Susceptibility Factor ^a	Fluidity Index
Colombian, 53 penetration at 25° C.	70	3.83	81
Healdton, 55 penetration at 25° C.	73	6.11	..
Midcontinent, 50 penetration at 25° C.	63	3.92	85
West Texas, 50 penetration at 25° C.	63	5.88	70

^a Penetration at 25° C.
Penetration at 0° C.

Thus, any theoretical consideration or comparison of asphalts must take into account these differences in behavior. In practice, certain uses demand a highly susceptible asphalt at elevated temperatures while, in other cases, the low-temperature characteristics are more important.

In applying the proposed methods of measuring susceptibility as an aid in choosing the proper asphalt for a given service, the fact should be borne in mind that susceptibility is by no means the sole criterion upon which the quality of an asphalt is based. Other properties, such as resistance to weathering, water absorption, or resistance to acid and alkali, for example, are usually just as important as susceptibility.

In the presentation of the results of this study, no attempts have been made to establish definite limits to any of the indexes or factors for the purpose of defining quality or suitability of an asphalt for any particular use. More practicable methods than those now in use are suggested, by which the consumer will be able more accurately to correlate his data on service behavior in so far as susceptibility is concerned. These methods have the advantages of covering a wider range of asphalts and conditions than was heretofore possible, and

employing apparatus and tests which are commonly used and hence familiar to those in asphalt work. The correlation between service behavior and the susceptibility as determined by the suggested methods should then serve as a guide for future decisions on the suitability of an asphalt for a given purpose. At the present time, the lack of reliable actual service data prevents the authors from giving any specific examples of this correlation in any one field.

In addition, it is hoped that the present contribution will serve as a basis for further thought and experimentation on the subject of susceptibility, which will undoubtedly result in a still greater appreciation of this characteristic of asphalts.

Conclusions

No single factor has thus far been evolved which will adequately express the temperature susceptibility of an asphalt over the wide range of temperatures encountered in the commercial application of asphalts.

Present methods are not entirely suitable, because they are too limited in the range of consistencies over which they can be determined or require the use of apparatus and testing methods not commonly used or recognized as standards.

A combination of factors or indexes is suggested by which a definite measure of the temperature susceptibility characteristics of a wide range of asphalts can be determined. The softening point-penetration index indicates this characteristic over a narrow range of normal atmospheric temperatures, the ratio of penetration at 25° C. to penetration at 0° C. at subnormal and the fluidity index at elevated temperatures.

These methods are equally applicable to straight reduced and oxidized asphalts and are easily determined by means of tests which are in common use.

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RECEIVED May 11, 1935. Presented before the Division of Petroleum Chemistry, Symposium on Asphalt, at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935.

Control of High Lights in Reading Microbalance Swings

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THE magnifying lens used in the balance case for observing the pointer of a microbalance, which is not provided with a telescope, is necessarily of high power and therefore gathers light from a large area. In cases where special arrangement for the illumination of the balance is limited, owing to the use of the room for other apparatus, it frequently happens that disturbing highlights from distant light sources are reflected by the lens into the eye of the observer.

A very simple device has proved to be a great assistance in overcoming trouble from ill-arranged light sources. It consists of a 10- or 12-inch square of dark cardboard (preferably,

but not necessarily, dull black), with a 1-inch circular hole in the center. By holding this card in the hand between the balance case and the observer the highlights are almost totally eliminated, the necessity of closing one eye is removed, and the balance is, in a measure, protected from the hot breath of the observer.

The device serves equally well in correcting faulty lighting conditions for ordinary analytical or assay balances which are provided with a magnifying lens in the balance case.

RECEIVED December 13, 1935.

Determination of Gaseous Olefins or Hydrogen by Catalytic Hydrogenation

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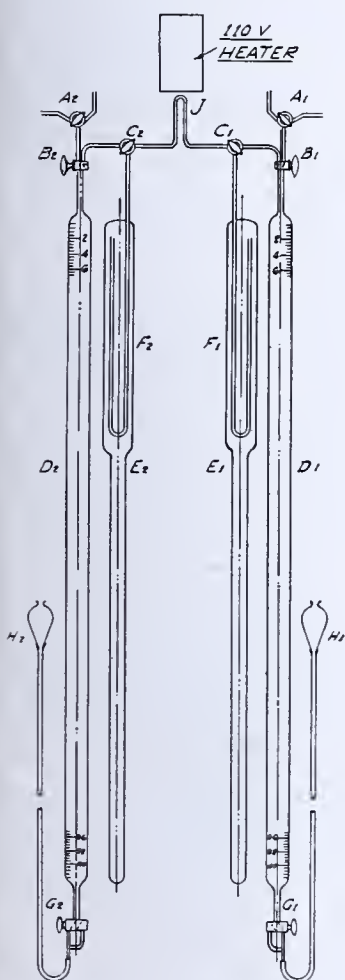


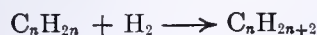
FIGURE 1. DIAGRAM OF APPARATUS

nearing saturation, or with changes in temperature. In addition, reagents for the determination of olefins are corrosive and volatile, necessitating unusual precautions and auxiliary reagents.

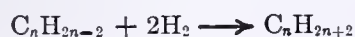
Proposed Method

A new method for the quantitative determination of gaseous olefins by catalytic hydrogenation, which has been developed in this laboratory and used for the past three years, gives consistent reproducible results accurate to a few tenths of a per cent in a time comparable with that of any liquid reagent method.

It requires only that a measured volume of hydrogen be mixed with a known quantity of olefin-containing gas and the mixture passed over a suitable catalyst at room temperature and substantially atmospheric pressure. The resulting contraction in volume is a direct measure of the amount of olefin present according to the reaction:



Thus, one volume of olefin reacts with one volume of hydrogen to form one volume of paraffin, and the change in volume on hydrogenation is from two volumes to one. In the case of acetylene or diolefins, the contraction is twice the volume present according to the reaction:



EXISTING methods for the analysis of olefinic gases may properly be divided into two classes: those using sulfuric acid, and those using bromine, but both depending on the reagent to react selectively with the olefins, leaving untouched any paraffins or cyclics present. For accurate work this is an admitted impossibility, even when the gaseous mixtures are separated by low-temperature fractional distillation and the resulting fractions are analyzed separately. Corrections must still be applied, which are at best rather doubtful, since these so-called selective reagents possess, in common with all absorption media, the undesirable ability to take up varying amounts of substances, other than the one they are being applied to absorb, and then to regenerate a portion of the dissolved constituents when used with another gas of different composition, when

Suitable corrections must be applied if present with olefins. The only two compounds likely to be found are acetylene and butadienes, and these can be determined separately by saturated potassium mercuric iodide (3) and maleic anhydride (11), respectively.

Typical results on synthetic samples of propylene in propane are shown in Table I.

TABLE I. ANALYSIS OF PROPANE-PROPYLENE MIXTURES

Run No.	Propylene %	Difference from True Per Cent
Sample 1 as synthesized	10.5	...
1	10.4	-0.1
2	10.4	-0.1
3	10.4	-0.1
4	10.7	+0.2
5	10.5	...
6	10.6	+0.1
Sample 2 as synthesized	50.5	...
1	50.6	+0.1
2	50.4	-0.1
3	50.5	...
4	50.5	...
5	50.5	...
6	50.3	-0.2
7	50.5	...

During the development of the method, similar consistent quantitative check runs were made using ethylene, propylene, individual and mixed butylenes, hydrogen, and acetylene. With only a few exceptions out of the hundreds of runs made, the results were not more in error than the possible accuracy of measurement of 0.05 ml. of gas.

Apparatus

The apparatus used, as shown schematically in Figure 1, consists of two complete Bureau of Standards (8) water-jacketed buret and compensator assemblies with a catalyst tube mounted between them. A heater is provided for catalyst preparation and regeneration.

The catalyst is prepared by melting about 4.0 grams of c. p. nickel nitrate hexahydrate in its own water of crystallization in a 50-cc. porcelain evaporating dish. Shredded long-fiber asbestos, which has previously been digested with hot nitric acid, washed, dried, and ignited, is then added until all the solution is absorbed. Any excess solution is pressed out with a porcelain spatula and drained from the evaporating dish. The nickel-saturated asbestos is then lightly calcined with a soft Bunsen flame until part of it appears black and the remainder greenish yellow. After cooling, the mass is broken up into small pieces and added to a U-shaped catalyst tube of 8.0-mm. Pyrex glass to a depth of about 6.5 cm. on each side. Both ends are plugged loosely with ignited asbestos or glass wool and the glass tube is indented below the plugs to keep them in place.

The tube is then heated to not over 310° C. while slowly drawing laboratory air through it with the vacuum line. This is continued until no further brown fumes are evolved and the whole mass becomes entirely black.

The catalyst tube is cooled, connected to the apparatus, and flushed with hydrogen. It is then heated in a current of hydrogen to not over 325° C. for several hours and finally allowed to cool with the hydrogen still passing over it. The catalyst should be protected against air at all times to avoid poisoning.

When poisoned it should be flushed with hydrogen and reheated in that atmosphere to 325° C. When cooled the activity will be restored.

Procedure

It is assumed that the catalyst tube, J, has been activated as described above and that the manifold from B₁ to B₂ is filled

with hydrogen to protect it. Accordingly, with the mercury in the leveling bulbs and burets at the same level, the gases in manometers F_1 and F_2 are drawn into their respective burets, the contents of which are then discarded to the atmosphere.

Connection is then made from A_2 (left-hand buret) to a cylinder of pure hydrogen through a suitable reducing valve. After thorough purging through A_2 , the cock is opened to the buret and 70.0 or 80.0 ml. of hydrogen are drawn into D_2 . Cock A_2 is again closed, C_1 is opened to J , F_1 , and B_1 , and B_2 is carefully opened, allowing the hydrogen to level manometer F_1 by filling it until the mercury almost touches the electrical contact, then reversing G_2 to slow down the rate until contact is shown by the right light flashing; at which point G_2 is quickly closed and then C_1 is closed to F_1 but opened to J and B_1 . Manometer F_2 is ordinarily left filled with mercury. After C_1 is closed to F_1 , the remaining hydrogen is flushed out the tail of cock B_1 . B_2 is then reversed and mercury brought to A_2 as before.

The apparatus is now ready for an analysis. Pure hydrogen is again added through A_2 until about 50.0 ml. are taken, although the amount of hydrogen required depends on the sample. Preferably about twice as much hydrogen is taken as is required; acetylene and diolefins, of course, require twice as much hydrogen as olefins. A_2 is then closed and B_2 opened to the manifold. With the levels in H_2 and D_2 approximately equal, C_1 is opened toward B_2 , F_1 , and J , and the mercury in F_1 brought to the contact point by adjusting H_2 . The balance is always obtained by allowing the mercury to flow upward toward the platinum point—never the reverse. At that point, G_2 is quickly closed and the reading taken for "hydrogen added."

Approximately 50.0 ml. of sample are taken into D_1 in a similar manner, except that C_1 is opened toward B_1 before B_1 is reversed. After F_1 is set, G_1 is quickly closed and the amount of "sample" noted.

With C_1 opened, the mercury in F_1 is pulled up until it just touches the cock, which is then closed to the manometer. This step is important and should not be neglected. With G_1 and G_2 opened full, the hydrogen in D_2 is passed into D_1 and the gases are thoroughly mixed by alternately raising and lowering H_2 and H_1 from three to five times.

Both cocks are then partially closed so that the speed is reduced to about 2.0 minutes per pass each way. After five complete passes, the mercury in buret D_1 is raised to cock B_1 which is then closed. H_2 and D_2 are approximately balanced, and C_1 is carefully opened under a little pressure to the manifold and B_1 . The mercury level is set to the point in F_1 , the level is read in D_2 , and the contraction noted.

Successively, two additional complete passes over the catalyst are made and the contraction is again noted until the volumes remain constant.

In the case of olefins or hydrogen, the loss in volume is a direct measure of the amount present. In the case of acetylene or diolefins, the shrinkage is twice the amount present.

After each analysis, tube J should be flushed with hydrogen and the manifold isolated to protect the catalyst against poisoning by air.

For the determination of hydrogen in fixed gas cuts or "total unsaturation" in gases containing relatively large amounts of carbon monoxide, it is necessary to heat the catalyst to 180° C. and pass the hydrogenation mixture over it at that temperature. Operation in such cases is exactly as at room temperature except for heating the catalyst and allowing time for cooling before the contraction is noted. At the end of such determinations, it is necessary to purge the catalyst with hydrogen and heat it to 310° C. before using again at room temperature. Such regenerations take about 10 minutes and do not impair the activity of the catalyst. If used only at 180° C., activation between runs is not necessary. The presence of hydrogen or olefins in the original gas does not affect the determination but does reduce the amount of auxiliary gas necessary to be added.

Oxygen, if present, must be removed or determined since it is also hydrogenated and hence must be considered in the subsequent calculations.

Comparison of Methods

During preliminary work on the problem, a complete test was made of the usual reagents for the determination of both total and individual olefins. Sulfuric acid in varying strengths

and containing various recommended catalysts (4, 5, 10) bromine and bromine water, silver nitrate, dichromates, permanganate, chromic acid, cuprous sulfate, β -naphthol, and several other reagents were tested but the results were not satisfactory. Absorption was either incomplete or the reagent also attacked the paraffins. In some cases, corrections, when applied, yielded good results for individual olefins but poor results for mixtures. The conclusion of the tests was that none of the present liquid reagents was satisfactory for reliable quantitative work but that saturated bromine water in 2 to 1 dilution, and 30 per cent fuming sulfuric acid were probably the two best, particularly for the determination of total unsaturation. Accordingly, at the end of the development of the hydrogenation method, a comparative test was made between it and the two best reagents.

Experimental

PARAFFINS. The paraffins, ethane, propane, and butanes were commercial gases which had been thoroughly purified by successive chemical scrubblings through 30 per cent fuming, 98 per cent, and 79 per cent sulfuric acid and 54 per cent potassium hydroxide, then passed through soda lime and dried by anhydrous. They were fractionated and refractionated through a special precision low-temperature distillation column (?) discarding both end fractions until the whole of the material had a constant boiling point and the end fractions on distillation showed the same vapor pressure when tested in a Shepherd differential manometer.

ETHYLENE. Ohio Chemical "anesthetic" ethylene was scrubbed through 90 per cent sulfuric acid, then fractionated and treated the same as the paraffins.

PROPYLENE. After several fractionations failed to separate a small amount of propane impurity from commercial propylene, the redistilled mixture was brominated at -50° C. and the propylene regenerated from the dibromide by zinc dust in ethyl alcohol after fractionation of the dibromides. It was then fractionated the same as ethylene.

BUTYLENE. α -Butylene was prepared by the method of Lucas and Dillon (6), then refractionated to constant boiling point and vapor pressure.

ACETYLENE. Commercial acetylene was scrubbed through water, cuprous chloride solution, dilute acid and caustic, dried, and refractionated several times at 1.5 atmospheres' pressure.

Synthetic Mixtures

For the comparative test, nine synthetic mixtures of accurately known composition were made in a calibrated and carefully evacuated all-glass system by blending by condensation, ethylene with ethane, propylene with propane, α -butylene with isobutane, and acetylene with ethane. These samples were representative of the corresponding cuts made in low-temperature fractional distillation. Each mixture was then analyzed successively by each of the three methods.

TABLE II. COMPARATIVE TESTS

Sample No.	True Per Cent	Proposed Hydrogenation Method %	Sulfuric Acid Method %	Bromine Method %
1E	5.4	5.2	9.0	7.3
1P	6.5	6.5	7.8	7.3
1B	6.6	6.4	9.3	7.1
2E	46.9	47.1	54.5	47.5
2P	48.6	48.9	48.6	48.8
2B	49.8	49.9	47.9	50.9
3E	69.3	69.6	68.0	66.8
3P	73.2	73.2	73.8	74.0
1A	40.8	40.6	41.0	40.0

Both the sulfuric acid and bromine runs were made in six pass cycles followed by three passes into caustic for both, and one pass into alkaline pyrogallol for the bromine runs. A U. S. Steel Corporation (1) apparatus with Francis auto-bubblers was used for all reagents.

Results on the reagent methods were calculated, except for 1B and 2B by the sulfuric acid method (Table II), by subtracting the product of the number of cycles times the

constant contraction from the total absorption, multiplying by 100, and dividing by the sample volume. Both the butylene mixtures (1B and 2B) showed no constant contraction in acid but continued to react until the samples could no longer be measured. Corrections for these samples were calculated by the method of Sullivan (9). The corrected results are shown in Table II. Catalytic hydrogenations were made as described, no corrections being necessary.

It is apparent that the hydrogenation method gives consistently the best results even when corrections are applied for the secondary reaction and solubility effects of the liquid reagents. The magnitude of the corrections and the number of passes to constant contraction are shown in Table III. The acid values for 1B and 2B are based on 12 passes only, and not on constant contractions.

TABLE III. CORRECTIONS BASED ON CONSTANT CONTRACTIONS

Sample No.	Acid		Bromine	
	Passes	Correction Ml.	Passes	Correction Ml.
1E	30	- 8.0	36	-2.4
1P	36	-15.0	24	-3.4
1B	12	-15.5	36	-0.9
2E	36	- 4.8	36	-1.2
2P	24	- 6.4	30	-2.5
2B	12	-13.7	30	-2.0
3E	24	- 3.2	36	-2.4
3P	36	- 4.8	30	-1.0
1A	18	- 2.1	48	-4.0

Even a casual comparison of Table III shows that the corrections for low olefin concentrations may exceed the amount of unsaturate present and that without applying some such correction both reagents are worthless for exact work.

In the light of work by some other investigators, the use of such strong acid was admittedly a doubtful procedure, but the results with it were no worse than those which would have been obtained for ethylene if some other weaker acid had been substituted. The choice of 30 per cent fuming acid was made after careful tests on mixed olefinic gases where it gave better results, after corrections were applied as outlined, than any of the weaker acids and in less time. For the individual cuts, weaker acids reacted less with the paraffins but the results were little, if any, more satisfactory. The "selective" absorption of individual olefins from a mixture by increasing acid concentrations was totally unsatisfactory, as has been found by other investigators (2).

TABLE IV. DETERMINATION IN SYNTHETIC MIXTURES

	Mixture I		Mixture II	
	Synthesized	Found	Synthesized	Found
Carbon dioxide, %	3.2	..	5.0	..
Oxygen, %	0.4	..	None	..
Carbon monoxide, %	6.3	..	26.0	..
Hydrogen, %	41.7	41.8	12.4	12.4
Ethane, %	48.4	..	56.6	..
Hydrogen sulfide, grains per 100 cu. ft.	13.0	..	10.0	..

In spite of the increase in accuracy by the hydrogenation method, it requires only about the same time as the reagent methods. Five 4-minute cycles over the catalyst are almost always sufficient for completely hydrogenating 50.0 ml. of olefins, which is the largest sample usually taken, and only three volume readings are necessary in the whole analysis.

The absorption methods, though requiring less time per pass, take more time because of the larger number of passes necessary to constant contraction and the large number of volume readings. For control work, rapid determinations can be made in 12 minutes on as little as 10 cc. of gas with an accuracy comparable with usual reagent methods.

The method is equally applicable to the determination of hydrogen in refinery and manufactured gas. In such cases the catalyst should be used at 180° to 195° C., at which temperature it is active in the presence of any amounts of carbon monoxide, and any pure olefin is added instead of hydrogen. This is shown in Table IV for two synthetic mixtures of gas similar to manufactured gases encountered in practice.

Application

The method is now being used in this and other laboratories for the determination of total unsaturation and of hydrogen, and in conjunction with low-temperature fractionation to give a complete analysis of refinery and cracked gases. In spite of rough usage and exposure to gases containing sulfur compounds up to approximately 60 grains per 100 cubic feet, calculated as hydrogen sulfide, no catalyst failures have occurred in over 3 years. Typical check results on two routine plant gases separated by fractional distillation and then hydrogenated are shown in Table V.

TABLE V. CHECK RESULTS ON PLANT GASES

	Reformed Gas		Absorption Gas	
	%	%	%	%
Oxygen	0.1	0.1	None	None
Carbon dioxide	None	None	None	None
Carbon monoxide	None	None	None	None
Hydrogen	11.5	11.3	6.3	6.3
Methane	20.5	20.7	45.5	45.5
Ethylene	16.9	16.8	3.1	3.0
Ethane	8.6	8.8	24.5	24.6
Acetylene	1.2	1.1	None	None
Propylene	20.9	20.9	5.0	5.0
Propane	16.8	16.8	12.6	12.6
Isobutane	0.2	0.2	0.6	0.5
Iso + 1-butene	1.8	1.7	0.4	0.6
N-Butane	0.5	0.5	0.8	0.7
2-Butenes	1.0	1.1	0.3	0.3
Butadiene	None	None	Trace	Trace
Pentanes and heavier	None	None	0.9	0.9
Total unsaturation (on original sample)	42.8	42.8	9.1	9.0

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Fluidity and Hygroscopic Properties of Shellac

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WHENEVER shellac is to be used as a thermoplastic material, its degree of fluidity when heated is an important consideration, and may also furnish information about the age or past history of the resin. When shellac is heated, it gradually loses water with a corresponding loss of its plastic properties. This same change takes place, though much more slowly, at ordinary temperatures. It has been shown that the thermoplasticity can be restored by heating polymerized shellac with water under pressure (5); however, in this case certainly some secondary reactions take place as well as a hydration, since the iodine number is increased.

To measure the fluidity under heat, three methods have been used, two of which are today in regular commercial use. In the so-called Victor test (3) the sample is not subjected to any previous conditioning, but is tested in its normal state, being merely ground to 20-mesh. For the Westinghouse or Metropolitan-Vickers test (4), the sample is placed in a desiccator over calcium chloride for 48 hours before testing. Recently Committee D-9 of the American Society for Testing Materials has been working on a modification of the V-tube method (1), which recommends that the sample be conditioned by heating for 16 hours in a well-ventilated oven at $41^{\circ} \pm 2^{\circ} \text{C}$. The results obtained by different laboratories with the three methods have not checked each other particularly well.

Some time ago it was of interest to the authors to measure the hygroscopic property of shellac and note the effect on flow. Experiments were carried out on several shellacs, and the following series, obtained in using an ordinary superfine grade, is typical:

After grinding to 30-mesh, about 5-gram samples were spread out in thin layers in desiccators of constant humidity, held at room temperature (about 27°C , 80°F .). The humidity regulators were concentrated sulfuric acid (0.0 per cent humidity), 45.8° Bé. sulfuric acid (25.0 per cent humidity), 36.5° Bé. sulfuric acid (50.0 per cent humidity), saturated ammonium chloride solution (79.3 per cent humidity), and water (100 per cent humidity).

The samples were weighed daily until they came to constant weight, which occurred in about 5 days. Weighings were continued for several days more in order to get check readings, after which the samples were transferred to an ordinary concentrated sulfuric acid desiccator and dried to constant weight. Finally the weights of the containers were taken.

It took considerable time for a sample to come to equilibrium in the moist atmosphere. However, particularly in the case of the two high humidities, changes took place with sufficient rapidity, whenever the sample was removed to balance, to make accurate weighing difficult. The results

obtained have been plotted in Figure 1. It is of interest that when the sample which had been dried over concentrated sulfuric acid was removed to an ordinary drying oven for 24 hours and held at 41°C ., it picked up 0.37 per cent moisture.

The equilibrium moisture in the experiments described above is believed to represent merely adsorbed water attracted by the free hydroxyl groups of the shellac. Gardner (2) has shown that shellac varnish films are permeable to water vapor, and also absorbent to moisture. These films were formed by the evaporation of a solvent, and might conceivably be in a different physical condition from lac in its native state—that is, the secretion of the lac insect—or in the manufactured condition, as shellac. In this latter case, also, the progressive adsorption of moisture with increasing humidity found in the authors' experiments is in accordance with the assumption of a relatively porous structure.

Samples duplicating those described above were prepared and tested for Victor flow, after coming to equilibrium at the humidities mentioned. In this test the measure of fluidity is the distance in millimeters which the molten shellac flows down an incline of 15° to the horizontal in exactly 12 minutes at a temperature of 100°C . The flow of the original sample was 48 mm. The results obtained are given in Table I, which shows the very great effect of a small amount of adsorbed water on the fluidity, as measured by the Victor method. Attempts to bring back the fluidity of a "dead" lac—that is, one which possessed zero flow under ordinary conditions—by exposing it to the action of a high humid atmosphere were unsuccessful.

TABLE I. VICTOR FLOW TEST

Humidity %	Absorbed Moisture %	Flow Mm.
0.0	0.00	19
25.0	0.89	28.5
50.0	1.46	46
79.3	2.48	65
100.0	4.79	103

Summary

These experiments show the marked hygroscopic nature of shellac and the need for specifying exactly the conditions of preparation of the sample in any method for determining the fluidity. It is recommended that the sample be conditioned previous to testing by exposure to 50 per cent relative humidity at room temperature, for three reasons: (1) In manufacturing operations shellac is used under ordinary atmospheric conditions which would average near this figure; (2) at this humidity equilibrium appears to be much more quickly established than at the higher or lower points; and (3) in weighing the sample less trouble is experienced than in the case of shellac conditioned at either high or low humidity. If the sample is prepared as described, at least 2 days should be allowed for the moisture content to come to equilibrium before testing for flow.

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RECEIVED December 2, 1935.

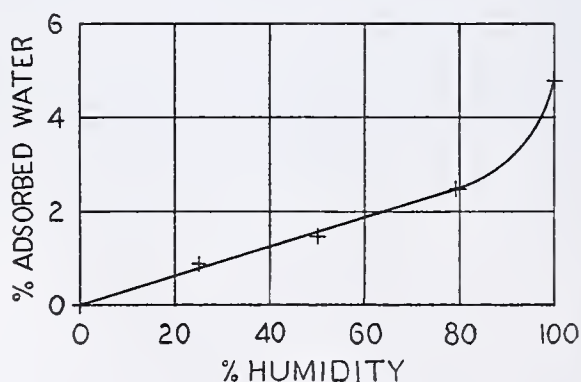


FIGURE 1

Determination of Selenium in 18-8 Stainless Steels

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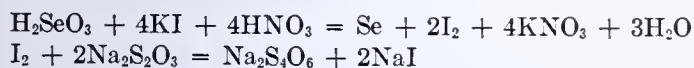
THE method used by the Carpenter Steel Company for the determination of selenium in 18-8 type steels has been the only available method. It depends upon solution of the steel in aqua regia, addition of perchloric acid, and evaporation to fumes to dehydrate silica. Solution of the perchlorates and chromic acid in water is followed by filtration to remove silica. Hydrochloric acid is added to bring the concentration to about 30 per cent, followed by addition of concentrated hydrochloric acid saturated with sulfur dioxide gas. After being allowed to settle for 3 hours at an elevated temperature, the precipitated selenium is filtered upon a tared Gooch crucible, washed, dried, and weighed. The crucible is then heated to redness, the selenium volatilized, the crucible reweighed, and the loss in weight represents the selenium present.

The manufacturer's analysis of the sample of steel used throughout this work was as follows:

C	Mn	P	S	Si	Cr	Ni	Se
0.11	0.83	0.137	0.009	0.50	18.29	8.99	0.218

The percentage of selenium was independently checked by an analysis carried out according to the directions furnished by the Carpenter Steel Company. The value is too high, in the light of further work, apparently because of certain positive errors which seem to be inherent in this method. Communication with industrial laboratories also showed that considerable difficulty was being experienced in getting satisfactory results in selenium determination.

The method developed in this laboratory depends upon solution of the steel in perchloric acid, catching the small amount of selenium which is evolved as hydrogen selenide, filtration of the solution to obtain the precipitate of selenium plus silica, and solution of the selenium in nitric acid, followed by the volumetric determination of selenium iodometrically, according to the equations:



The apparatus used consists of a 250-cc. Erlenmeyer flask with a one-hole rubber stopper carrying a 7.5-cm. (3-inch) drying tube, with the stem elongated and bent so that the tube is in a horizontal position.

The selenious acid used was prepared from pure sublimed SeO_2 and the concentration determined gravimetrically by precipitation of selenium with strong hydrochloric acid and sulfur dioxide. The thiosulfate used was approximately 0.01 *N*. The selenium titer of the thiosulfate solution was obtained by direct titration of this standard solution of selenious acid. Bureau of Standards sample No. 101, used for checking certain results, has the following analysis:

C	Mn	P	S	Si	Cu	Ni	Cr
0.061	0.554	0.011	0.013	0.763	0.056	8.44	17.56

Analytical reagent perchloric acid containing approximately 60 per cent of perchloric acid was used.

Procedure

Weigh a 5.00-gram sample of steel into a 250-cc. Erlenmeyer flask. Add a mixture of 50 cc. of 60 per cent perchloric acid and 30 cc. of water. (Somewhat less perchloric acid might be used to effect solution.) Insert the one-hole rubber stopper and drying tube. In the large end of the drying tube, place a pad of glass wool about 2.5 cm. (1 inch) long, lightly packed, and upon it pour 4 or 5 drops of concentrated nitric acid. Heat the

flask and contents to 80° to 85° C., remove from heat, and allow solution to proceed. At the end of about 2 minutes, remove the drying tube with the glass wool from the flask; solution of the steel will proceed without loss of any selenium as hydrogen selenide. Remove the glass wool, containing about 1 mg. of precipitated selenium, from the tube, place in a beaker, and wash out the tube with concentrated nitric acid into the beaker. To this nitric acid solution add the precipitate obtained by filtration of the main solution. Filter the main solution through a pad of asbestos with the aid of suction, and wash with warm water. Digest the pad of asbestos plus the dark-colored precipitate and the glass wool with about 40 cc. of concentrated nitric acid and evaporate the solution to a volume of about 10 to 15 cc. Make the solution slightly alkaline with ammonium hydroxide to precipitate small amounts of iron, filter, and wash the residue with hot water. The amount of iron is so small that the selenium carried down may be neglected. Make the clear filtrate just acid with nitric acid and add an excess of 10 cc. of concentrated nitric acid. Heat the solution to about 60°, add 3 grams of urea to eliminate small amounts of nitrous acid, and cool the solution to room temperature, to allow an iodometric titration. Bring the volume of the solution to 400 cc., add 3 grams of potassium iodide, allow to stand 1 or 2 minutes, and titrate the liberated iodine with thiosulfate, using starch as an indicator. The end point should last several minutes.

Experimental Data

Because it was impossible to obtain a standard sample of steel containing selenium, it became necessary to examine carefully the gas evolved, the precipitates formed, and the main solution, in order to determine the percentage of selenium present. When hydrogen selenide is passed over glass wool containing a few drops of nitric acid, it is oxidized to red selenium, which is readily visible. This test is sufficiently sensitive to detect the hydrogen selenide evolved when 0.1 gram of selenium steel (0.19 per cent of selenium) is mixed with 5.0 grams of Bureau of Standards steel No. 101; thus the method will detect 0.2 mg. of selenium.

Using this test, it is evident that hydrogen selenide is evolved when a selenium steel is treated with dilute perchloric acid, but this evolution lasts for only a few minutes while the steel starts to go into solution. Once the steel is reacting vigorously the hydrogen selenide ceases to be evolved. With concentrated perchloric acid (approximately 60 per cent) no hydrogen selenide is evolved. The reason for this experimental fact has not yet been established.

In order to test whether the glass wool moistened with nitric acid caught all the hydrogen selenide, the following method was used:

Two bubble tubes, each containing 25 cc. of concentrated nitric acid, were connected to an Erlenmeyer flask containing the selenium steel and dilute perchloric acid. The evolved gas was bubbled successively through the tubes until the steel was completely dissolved. An examination of the two nitric acid solutions showed that the first tube caught all the selenium; none was found in the second tube. Therefore, the tube of glass wool plus nitric acid was inserted in the neck of the flask and connected to a bubble tube of nitric acid. After solution of a 5.0-gram sample of selenium steel with this arrangement, no selenium was found in the nitric acid of the bubble tube, proving that the glass wool plus nitric acid caught the hydrogen selenide which was evolved.

The tube containing the glass wool, nitric acid, and red selenium was added to the remaining selenium in the precipitate. Approximately 1 mg. of selenium was evolved as hydrogen selenide when the recommended concentrations of perchloric acid are used.

The solution, containing a dark red to black precipitate of selenium together with about four-fifths of the silica, was filtered on a pad of asbestos, supported by about 1.3 cm. (0.5 inch) of wool felt and a perforated porcelain plate, using the tall-form straight-sided Gooch funnel. After filtering and washing three or four times with warm water, a glass rod was pushed up through the

stem of the funnel against the porcelain plate and the entire pad forced to the top so that the asbestos layer plus the precipitate could be removed easily. The asbestos pad thoroughly cleaned the sides of the funnel, as it moved up. The asbestos pad was added to the glass wool and the entire mass treated with concentrated nitric acid, as described above.

After filtering out the precipitate, it was necessary to examine the filtrate for selenium. To this filtrate, a volume of about 100 cc., were added 125 cc. of concentrated hydrochloric acid which had been saturated with sulfur dioxide. The solution was allowed to stand for 2 hours; upon filtering no selenium was found. Therefore, to this solution was added a definite quantity of selenious acid, equivalent to 1.14 mg. of selenium. After standing 2 hours, the solution was filtered and the amount of selenium obtained checked with the amount added, showing that the solution was initially in the proper condition for the precipitation of selenium.

Samples of Bureau Standards steel No. 101 were dissolved in 50 cc. of perchloric acid plus 30 cc. of water and a definite amount of selenium (1.14 mg.) was added in the form of selenious acid. Upon precipitation with hydrochloric acid and sulfur dioxide the correct amount of selenium was found present, showing the accuracy of the iodometric method.

Using the method as outlined on the manufacturer's sample (reported as 0.218 per cent of selenium) the following representative values were obtained: 0.190, 0.191, 0.191, 0.188, 0.193, 0.192, 0.193, 0.188, 0.189, and 0.190 per cent of selenium. These percentages all reduce to 0.19 per cent when two significant figures are reported, as is customary in steel analyses.

The manufacturer's sample was diluted with an equal quantity of Bureau of Standards sample No. 101. An analysis of this diluted sample by the recommended procedure gave values of 0.094 and 0.094 per cent of selenium.

Since experiments showed that no hydrogen selenide was evolved by 60 per cent perchloric acid, a sample of selenium steel was dissolved in this strength of acid, by heating to about 85° C. After complete solution of the steel, 125 cc. of concentrated hydrochloric acid saturated with sulfur dioxide were added. After standing for 2 hours the precipitate was filtered, washed, dissolved in nitric acid, and carried through the volumetric procedure as described, to give 0.190 and 0.191 per cent of selenium. These results indicate an alternate procedure for the determination of selenium and furnish a check upon the procedure given.

The method of the Carpenter Steel Company was employed on samples of selenium steel and carried to the point where the precipitated selenium was filtered upon a Gooch crucible. At this point, the precipitate was carried through the volu-

metric procedure and 0.190, 0.193, and 0.194 per cent of selenium were obtained, furnishing additional corroboration of the procedure given.

As for interfering constituents, Bureau of Standards steel No. 101 was carried through the recommended procedure and gave a blank result. It might be expected that a small amount of copper could remain in the insoluble residue and then react with hydriodic acid to yield iodine, but the fact that negative results were obtained in the blank experiment was considered sufficient proof that selenium alone was measured by this volumetric method.

For routine work, the procedure could be materially shortened by eliminating the use of the glass wool and applying a correction factor of about 0.5 mg. for the selenium which is evolved as hydrogen selenide. Also the precipitation and elimination of small amounts of iron by ammonium hydroxide could possibly be eliminated in routine steel analyses.

Conclusion

The procedure given is fairly rapid. A series of 5 samples was analyzed simultaneously in 1.5 hours. The accuracy has been checked by two procedures, and seems adequate. The values are lower than those obtained by the original method of the Carpenter Steel Company, but an examination of the gravimetric method, for such small amounts of precipitate, led to the conclusion that it yields slightly high results.¹

Acknowledgment

The need for a method for the determination of selenium in 18-8 type steels was first suggested by G. E. F. Lundell of the Bureau of Standards to L. F. Hamilton of the Analytical Division of the Department of Chemistry of this institute, at the latter's request. The authors undertook the investigation after communicating with Berton H. DeLong, metallurgist for the Carpenter Steel Company, Reading, Pa., manufacturers of the type of steel to be investigated. Mr. DeLong very kindly furnished the material for analysis and generously offered to cooperate in every way possible.

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¹ In a private communication from the Carpenter Steel Company, it is stated that "our figure of 0.218 per cent of selenium is from a routine heat analysis obtained in our control laboratory;" hence deviations in results of the magnitude observed are only to be expected.

An Efficient Laboratory Extraction Apparatus

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A SERIES of studies in this laboratory upon the constituents of various seeds has frequently met the problem of efficient extraction of large quantities of material. Metal apparatus was ruled out in order to avoid the possibility of contamination; various glass makeshifts proved leaky and inefficient. With low-boiling solvents such as acetone, petroleum ether, ethyl ether, etc., these difficulties became acute. Accordingly, a modified Soxhlet-type extractor (illustrated) was developed which can be duplicated at moderate expense from parts readily available. This model has been in use for the past year, and has given very satisfactory results. It is described here in the hope that it may prove helpful to others having similar problems.

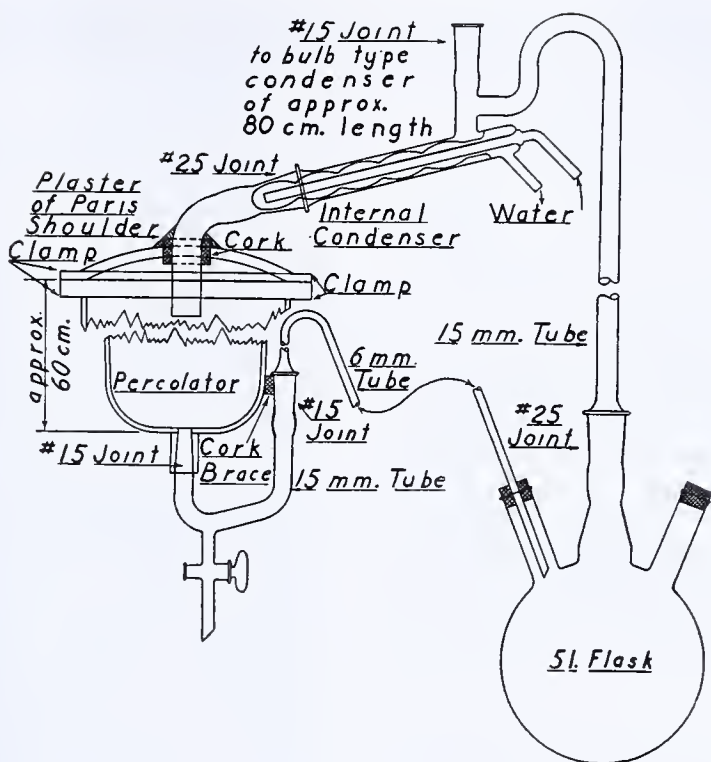
The extractor is made from a 7-liter Oldberg, or cylindrical, percolator and has a capacity of about 3 kg. of seeds. A percolator with a ground upper surface is selected, together with a small desiccator lid of the same diameter, and these are re-ground to a good fit. Next a large hole for the cork is cut in the lid, preferably with a cylindrical copper tool in a slow-speed drill press, using a rough grade of grinding compound. The main novel feature is an internal condenser which cools and liquefies nearly all vapors before they pass into the percolator, thus reducing loss at the ground interface between the percolator and its cover. In operation, this interface is rendered more nearly solvent-tight by clamping it at two diametral points with large laboratory clamps as indicated. A second advantage gained from the use of an internal condenser is that uniform conditions of cold solvent extraction are maintained, often of value where sensitive crude materials are involved. The bulk of vapors is

condensed as in the usual Soxhlet extractor by the large Allihn-type reflux condenser (not shown).

The numerous potential leaks in such a set-up are avoided by substituting ground-glass joints for corks wherever possible. The joint connecting the siphon tube to the bottom of the percolator is ground in carefully by hand, first using discarded glass stoppers of suitable size and taper until a minimum of grinding is necessary to adapt the standard taper joint. The three corks do not cause trouble if they are of fine grain and coated with collodion.

A narrow cloth bag containing the material to be extracted occupies about four-fifths of the volume of the percolator but must not be allowed to pack the interior completely, if siphoning is to be effective. A channel is provided by inverting an 80-mm. evaporating dish over the bottom opening and placing several 10- to 15-mm. tubes along the full length of the side of the bag. These may be bent to conform to the curve of the percolator. The siphon tube extends only a small distance above the top of the bag, and must not be larger than 6 mm. in diameter if it is to fill properly. Sometimes the column fails to break completely after siphoning has stopped, causing the liquid to trickle over slowly. This prevents thorough extraction of the upper portion of material, and is caused by surface tension at the exit end of the siphon tube. It may be remedied by grinding off this end at a 45° angle.

The apparatus may be adapted to smaller charges than the maximum by inverting beakers or bottles within the percolator to occupy the excess space. It is most conveniently



mounted as a permanent assembly, lowering only the boiler and percolator for filling or emptying. The heat source will vary with the particular solvent used, but in most cases a water bath heated by an electric hot-plate is satisfactory. Where such a bath is used for long periods of time, the constant-level device of Wing (1) can be employed to advantage. The riser from the boiler may be insulated if desired.

Whereas the description here given provides for a 7-liter percolator of the Oldberg type, any of the percolators common in pharmaceutical technology might be employed with suitable modifications. The internal condenser in conjunction with ground-glass joints

wherever there is liquid or hot vapor is important in this design, whose details may be varied to suit individual convenience.

Acknowledgment

The writer wishes to thank R. A. Willihnganz for his cooperation in designing and constructing this extractor.

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A Rapid and Efficient Mixer

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IT IS frequently a time-consuming and tedious process to prepare for analysis samples of emulsions and plastics. The horizontal spiral-bit type of mixer has been successfully used in this laboratory and offers some distinct advantages over other methods of preparing such samples.

It is very easily assembled by attaching a spiral bit to the horizontal shaft of an electric motor, which should have a speed of 1725 r. p. m. and be rated at not less than 0.1 horsepower. A drill chuck obtained from any hardware store for approximately \$2 is mounted directly on the shaft. The diameter of the motor shaft must be specified in ordering the chuck. The spiral bit may be obtained from any hardware store for approximately 75 cents by specifying a 0.75-inch, solid-center, spiral bit. Before using this bit it is necessary to remove the tip, or worm, and the two cutters. The bit is then placed in the chuck. When the motor runs, the bit is turned in the opposite direction from that used when bor-

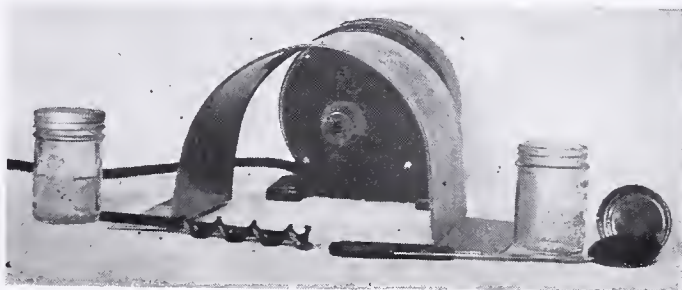
ing. This motion throws the sample into the bottom of the sample jar which is slipped over the bit. The jar is held in the hand and moved around to facilitate mixing. When the sample jar is withdrawn some particles of the sample may fly off, and are conveniently caught by a piece of tin shaped in a half-circle and placed on the bench over the bit.

The author's experience in using this mixer for preparing butter samples indicates the following precautions which must be observed:

Use a thick-walled glass sample jar with a screw cap, straight sides, flat bottom, and a capacity of approximately twice the volume of the sample.

Mix the sample for at least 3 full minutes. Since the butter can be mixed at temperatures from 12° to 25° C., the usual time required for properly tempering the sample can be eliminated.

Avoid partial separation of the sample due to melting around the edges of the sample jar.



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The Determination of Rhenium

II. The Geilmann Reaction

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THE Geilmann (2) color reaction for rhenium is brought about by adding hydrochloric acid, stannous chloride, and potassium thiocyanate to a solution of a perrhenate. The stannous chloride presumably reduces the rhenium to the hexavalent state where it reacts with the thiocyanate to yield an intensely colored complex. The actual compound formed is said to be $\text{ReO}(\text{CNS})_4$ (1, 9). Geilmann and co-workers have found that the lower limit of sensitivity lies somewhere in the neighborhood of 0.5γ per 10 ml. ($1\gamma = 0.001 \text{ mg.}$). The reaction has been adapted to the quantitative determination of rhenium in much the same manner as the corresponding molybdenum reaction has been utilized

in the Maag and McCollum (7) determination. Although molybdenum interferes when the Geilmann determination is applied directly to the analysis of minerals and concentrates, the method represents, with slight modification and when used in conjunction with a preliminary separation, the best available to date.

The procedure recommended by the original authors and similar to the analogous molybdenum method was as follows: To the nearly neutral solution of rhenium as the perrhenate were added 10 ml. of 20 per cent hydrochloric acid and 2 ml. of 10 per cent potassium thiocyanate. This was diluted to 50 ml. and treated with 10 ml. of 2 per cent stannous chloride. After shaking for 0.5 minute, 20 ml. of ether were added and the yellow complex was extracted. Residual traces of the complex were removed by a second extraction. It was early recognized that the intensity of color produced was dependent upon a number of factors. Chief among these were concentrations of reagents and time. By comparing the intensities of colors produced under varying conditions with the color of an aged ether extract of the complex, they were able to establish optimum concentrations and to arrive at what seemed to be the proper time interval between the addition of stannous chloride and extraction with ether. The reaction was apparently stopped by the addition of the extractor.

During the course of a series of analyses made in this laboratory (4) it became evident that the development of the color depended not only upon the concentration of the reagents but upon the amount of rhenium present. Likewise it was suspected that the reaction was not stopped by the addition of the extractor but continued in the nonaqueous solution at a greatly reduced rate.

The research herein reported was conducted in an effort to ascertain the magnitude and character of the color changes taking place during the course of the reaction and to establish if possible concentrations and time factors more favorable to analytical applications. The Eastman universal colorimeter, an instrument which has been previously described (5, 6) and used (3) in a research of this type, was used to follow color changes.

Experimental

Solutions used were similar to those of Geilmann, Wrigge, and Weibke (2). Potassium perrhenate solutions containing 10γ

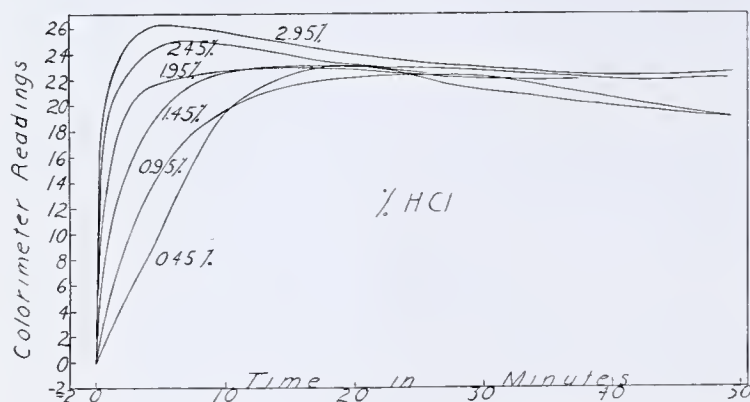


FIGURE 1

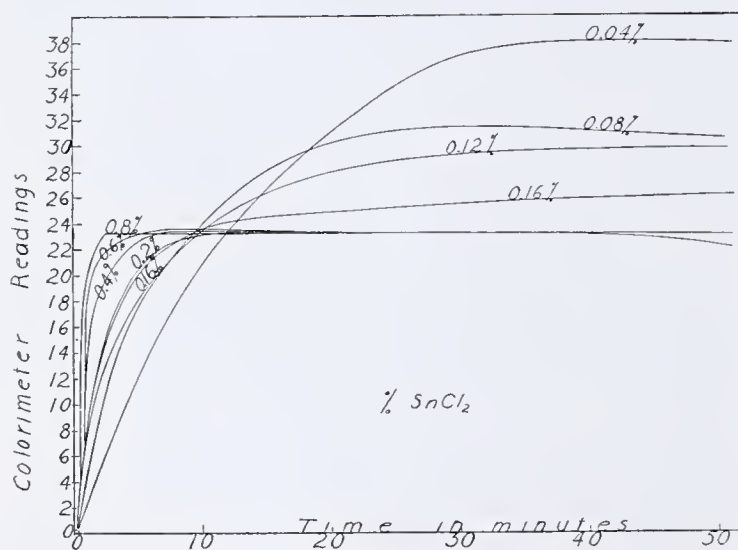


FIGURE 2

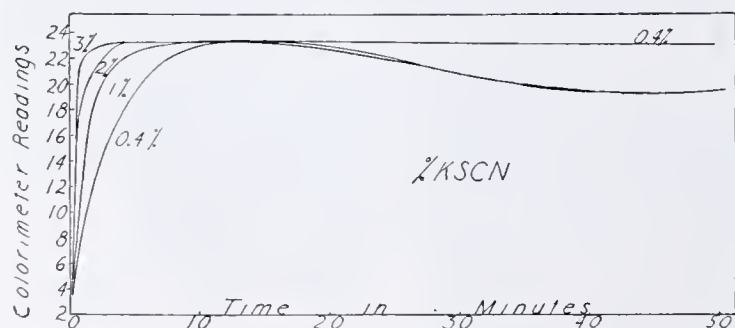


FIGURE 3

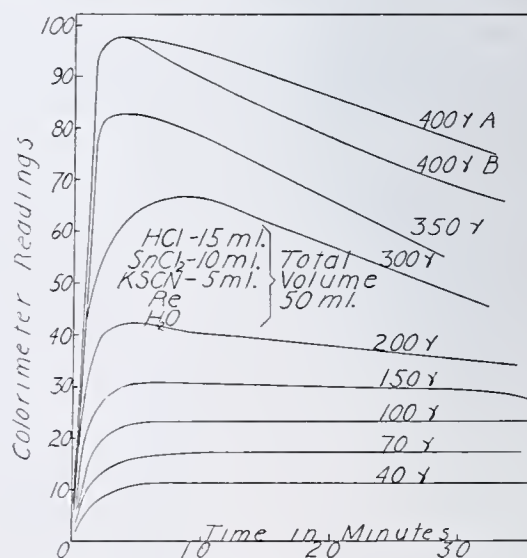


FIGURE 4

per ml. served as a source of rhenium. The procedure followed throughout was to run into the sample tube of the colorimeter a known amount of standard perrhenate solution. In a beaker were placed the desired amounts of hydrochloric acid, stannous chloride, potassium thiocyanate, and enough water so that the total volume of this solution and that of the perrhenate would equal 50 ml. The reagent mixture was then quickly mixed with the perrhenate solution and placed in the colorimeter. The time of mixing was taken as the zero time in all cases. The color changes were followed by the -blue wedge. When working with deeply colored solutions it was sometimes found necessary to make slight corrections with other wedges. All concentrations reported are on the weight basis.

Figure 1 illustrates the effect of varying the hydrochloric acid concentration in solutions containing 0.40 per cent of stannous chloride, 1.0 per cent of potassium thiocyanate, and 100 γ of rhenium. The percentage of acid includes that contained in the stannous chloride solution. In low acid concentrations the color did not reach a maximum until 20 minutes had elapsed. In the neighborhood of 2 per cent the color maximum was reached in 5 minutes, but fading took place over a period of 30 minutes. Figure 2 illustrates the effect of stannous chloride in a system containing 2.0 per cent of hydrochloric acid, 1.0 per cent of potassium thiocyanate, and 100 γ of rhenium. Low concentrations of the reagent developed the color slowly, but it is to be noted that at the end of 35 minutes the color with 0.04 per cent of stannous chloride was almost twice as intense as in a 0.8 per cent solution. In the latter concentration, however, the color maximum was quickly reached and remained practically constant over an appreciable period.

Figure 3 illustrates the variation produced by changing the potassium thiocyanate concentration in solutions containing 2.0 per cent of hydrochloric acid, 0.4 per cent of stannous chloride, and 100 γ of rhenium. Concentrations above 0.4 per cent produced a maximum color at the end of 5 minutes, whereas amounts in excess of 1 per cent promoted fading after 15 or 20 minutes. In Figure 4 are represented color concentrations produced by varying amounts of rhenium reduced in solutions containing 2.0 per cent of hydrochloric acid, 0.40 per cent of stannous chloride, and 1 per cent of potassium thiocyanate. Significant is the fading encountered in concentrations of rhenium much above 200 γ . Under the conditions of the experiment it would appear that 7 minutes is the optimum time interval before extraction. In the 400 γ region there is illustrated a phenomenon which has often been encountered in these laboratories and which may introduce serious error into a determination. Curves A and B represent the behavior of solutions containing exactly the same concentrations of reagents, the difference being that the solution represented by B was shaken vigorously for 1 minute before being placed in the colorimeter. Violent and prolonged agitation does not appear to shift the maximum but does promote more rapid fading of the color. In Figure 5 are plotted colorimeter scale readings against rhenium concentrations. Colors were developed in solutions containing 2.0 per cent of hydrochloric acid, 0.4 per cent of stannous chloride,

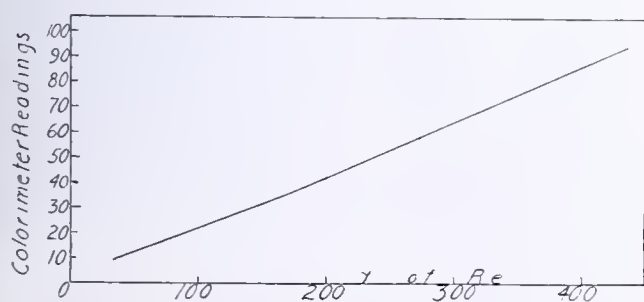


FIGURE 5

and 1 per cent of potassium thiocyanate. The time interval before extraction was 7 minutes.

The effect of stannic chloride was studied because in actual practice samples are often encountered which contain small amounts of oxidizing agents. These would oxidize the stannous chloride to produce significant concentrations of tetra-valent tin. Stannic chloride in concentrations as high as 2 per cent had little or no effect.

Nonaqueous Extractors

Butyl acetate, cyclohexanol, and ethyl ether have been used to extract the rhenium thiocyanate. The mixture of 65 per cent ethyl ether and 35 per cent petroleum ether as used by Malowan (8) for molybdenum extracts rhenium incompletely.

Because it had been suspected that nonaqueous solutions of the complex were not stable over a period of hours and that standards for comparison had best be prepared at the time of the analysis, a study was made of the behavior of these nonaqueous solutions. The color of 150 γ of rhenium was developed as described in the preceding paragraph, 7 minutes

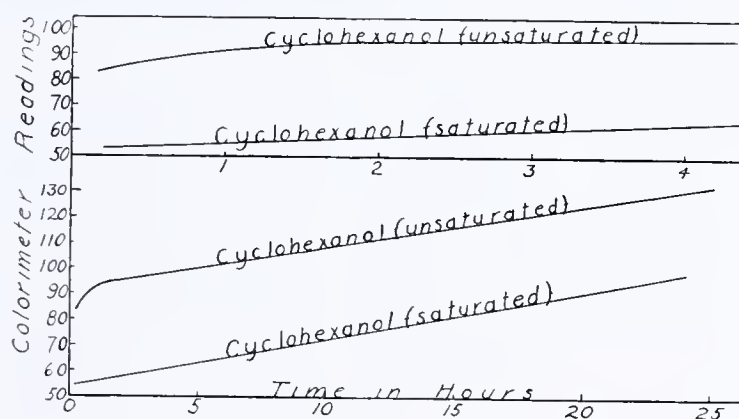


FIGURE 8

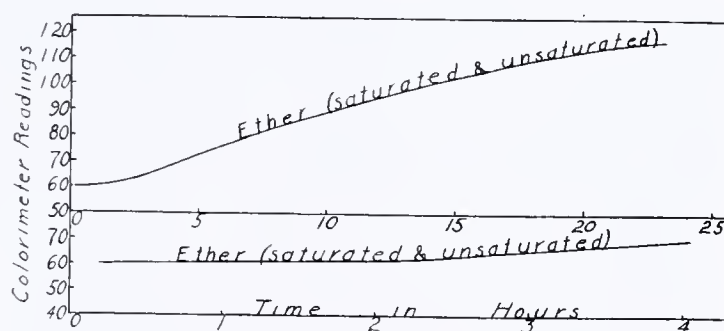


FIGURE 7

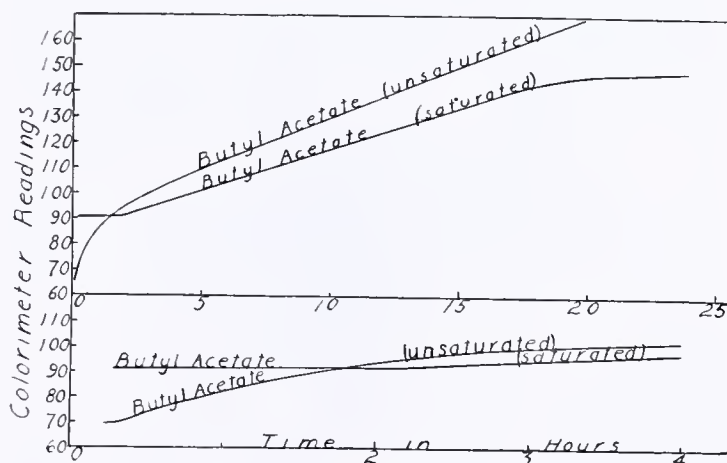


FIGURE 6

were allowed, and the extractor was added in three successive portions of 20, 15, and 15 ml. Extracts were then combined and placed in the colorimeter. The entire operation usually required about 12 minutes. Saturated extractors were prepared by shaking the extraction liquid in a separatory funnel just previous to use, with a hydrochloric acid, stannous chloride, and potassium thiocyanate solution of the same type as used in the actual analysis. Figure 6 illustrates the change in color of solution of 150 γ of rhenium (as the thiocyanate extract) in butyl acetate which had been shaken with the reagents and in untreated butyl acetate. It is apparent that the saturated extractor is preferable but that in neither case may it be assumed that such solutions constitute satisfactory semi-permanent standards.

Figure 7 is interesting in that it apparently makes little or no difference whether ether be saturated or unsaturated with respect to the reagents. However, erratic results are more often obtained in actual practice if the ether is not treated prior to extraction. This is in harmony with the findings of Geilmann and co-workers (2). Figure 8 is characteristic of cyclohexanol. The use of cyclohexanol eliminates to a large extent the peculiar results often obtained when ether is used as an extractor but has the decided disadvantage of separating slowly from the aqueous solution.

As a result of the study of the development of color in the Geilmann reaction it is recommended that when applied quantitatively to amounts of rhenium under 500 γ , the concentration of hydrochloric acid be held at 2.0 per cent, potassium thiocyanate at 0.4 per cent, and stannous chloride at 0.2 per cent. Seven minutes should in general elapse before extraction, and the solution should be shaken no more than is necessary to produce uniformity. Behavior of non-aqueous extractors has been studied and data are presented which indicate that such solutions do not constitute satisfactory permanent standards.

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RECEIVED August 10, 1935. Based upon the senior thesis of Bernard J. Babler, University of Wisconsin, 1935.

Separation of Stannic Oxide from Various Oxides by Ignition with Ammonium Iodide

Application to Analytical Purification of Ignited Stannic Oxide

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VOLATILIZATION of arsenic, antimony, or tin in the form of their chlorides from various compounds by gentle ignition with dry ammonium chloride was apparently first recommended as an analytical procedure by Rose (5). Rammelsberg (4) employed repeated ignition with ammonium chloride in a method for the approximate separation of stannic oxide from tungstic oxide. The conversion of stannic oxide into volatile stannic chloride in this way is, according to the authors' attempts, an impractical analytical procedure since an excessive number of successive ignitions are usually required. For example, in one experiment a sample of ignited stannic oxide weighing 0.5635 gram left a residue of 0.0127 gram of oxide after five successive ignitions with excess quantities of ammonium chloride. On the other hand it was found that ammonium iodide decomposes even highly ignited stannic oxide with great readiness, so much so that the amount of stannic oxide usually encountered in an analytical precipitate can be volatilized as iodide by a single ignition with ten times its weight of this ammonium salt. Since, at the temperature required for this volatilization, most of the other oxides likely to be found with tin oxide either are not attacked or are converted into relatively nonvolatile iodides which may be changed quantitatively back to the oxides, ignition with ammonium iodide can be used as a general method for the separation of stannic oxide from these others. At the time the present work was done it was thought that the analytical application of ammonium iodide in this manner was entirely new, but there was later located a single passing statement

by Moser (3) to the effect that metastannic acid could be separated from silicic acid by ignition with ammonium iodide. This present paper contains the results of experiments on the action of dry ammonium iodide at various temperatures on stannic oxide, ferric oxide, cupric oxide, lead oxide, nickel oxide, zinc oxide, antimony trioxide, tungstic oxide, and silicon dioxide, special attention being paid to the conditions for quantitative separations. As an example of the practical value of this general method there is given a rapid, convenient procedure for the determination of the exact stannic oxide content of ignited impure tin oxide precipitates, such as those obtained from the nitric acid treatment of common non-ferrous alloys.

Materials and Apparatus

J. T. Baker's reagent ammonium iodide was found to be sufficiently pure, particularly in regard to a low content of nonvolatile matter, to be used without further purification. One lot was found to leave no residue on ignition, while another contained an average of only 0.02 per cent non-volatile matter. Though it is desirable for such analytical work to have a reagent that leaves no weighable residue on ignition, it was found that satisfactory results could be obtained even with ammonium iodide of lower purity by allowing for a blank correction according to the purity of the chemical and the amount taken for an ignition. The various oxides were all prepared from pure chemicals by conventional methods.

Ordinary porcelain crucibles were used in the ignition experiments, and, while in a few cases a gas burner was used as

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the source of heat, the great majority of the trials were made in a small electric crucible furnace especially constructed for the purpose. By means of a suitable resistance this could be held constant within 5° throughout the working range, a nitrogen-filled thermometer with bulb placed next to the crucible being used to determine the temperature.

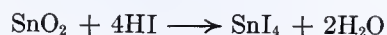
General Procedure

In the experiments on the oxides the dried weighed samples were first thoroughly mixed with ten or more times their weight of powdered dry ammonium iodide in weighed crucibles. Except where a gas burner was used, ignition was then performed at a controlled temperature by placing a charged crucible in the electric furnace previously brought to the desired degree of heat. After ignition was complete as shown by the cessation of fumes, usually requiring from 10 to 15 minutes, the crucible was removed. In some cases crucibles were then ignited in the open air in order to convert any residual iodide completely to oxide. In others, where slightly volatile iodides were present, the residues were first treated with small volumes of concentrated nitric acid, followed by evaporation to dryness on the hot plate in order to decompose the iodides completely before the final ignitions were made. Finally the crucibles were reweighed in order to determine the weights of residual oxide or oxides. Qualitative observations of the products of the reactions were also made.

Reaction with Stannic Oxide

While there is evidence of action at slightly lower temperatures, the reaction between ammonium iodide and stannic oxide does not proceed with sufficient velocity and completeness for practical analytical purposes until about 400° C. is reached. At this point there is rapid evolution of brown vapors of stannic iodide from the mixture, accompanied by white fumes of subliming ammonium iodide and the purple vapors of gaseous iodine. If the reaction is carried out at a sufficiently high temperature, the characteristic orange-red thermoluminescence of iodine can also be seen. It seems probable that the transformation of the oxide into iodide in this way is caused by the action of the hydrogen iodide that

results from the thermal dissociation of the ammonium salt. If this is the case the essential reaction can be represented by the equation



It is to be observed in support of this explanation that the order of the ease with which ammonium iodide and ammonium chloride react with stannic oxide is the same as that of hydriodic acid and hydrochloric acid, the latter having practically no action. That the reaction with these ammonium salts proceeds more readily in both cases than with the corresponding aqueous acids is in agreement with other reactions in which halogen halides at high temperatures react even more readily than their aqueous solutions with given substances, especially when water is one of the products of the gaseous reactions. The iodine appearing as one of the products of the reaction between ammonium iodide and stannic oxide apparently results largely from the thermal decomposition of the hydrogen iodide, although it is possible that a small proportion may come from its oxidation on contact with air. A possible alternative mechanism for the reaction is that it involves a direct action between the two substances as shown by the stoichiometric equation



Against this may be cited experiments on heating mixtures of finely ground potassium iodide and stannic oxide in which no evidence of any transposition reaction could be detected, though from the somewhat analogous nature of the two iodides one might expect at least some reaction in the case of potassium iodide if ammonium iodide reacts by a double decomposition reaction. Audrieth (1) cites evidence, however, that tends to show that fused ammonium salts can themselves behave like acids, and while no actual fusion takes place in the case discussed here, it is possible, in part at least, that the reaction between ammonium iodide and stannic oxide results from such a direct interaction.

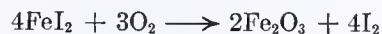
Reactions of Various Metallic Oxides

Since for purposes of practical analytical separation stannic oxide reacts too slowly below 400° C., little attention was paid to the behavior of the other oxides on ignition with ammonium iodide below this temperature. At 400° C. or above these are partially or completely converted into iodides, depending upon the temperature and the proportion of ammonium iodide. In general these other reactions appear to take place by the same mechanism as the stannic oxide reaction, except that in the case of ferric oxide and cupric oxide there are, in addition, oxidation-reduction changes.

The reaction with ferric oxide can be represented by the equation



By gentle ignition in the open air the ferrous iodide formed in this manner can be oxidized quantitatively back to ferric oxide according to the equation

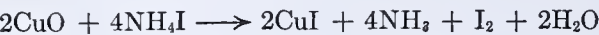


From the analytical viewpoint it was found that, if the treatment with ammonium iodide is carried out over a gas burner without much care as regards temperature control, the recovery of the ferric oxide is by no means quantitative, owing apparently to volatilization of some ferrous iodide during the ignition. By performing the ignition in an electric furnace at temperatures under 500° C. this loss does not occur, and recovery of all the oxide originally taken is then possible. From a practical manipulative standpoint the conversion of ferrous iodide to the oxide by simple air oxidation is not en-

When mixed with a suitable excess of powdered ammonium iodide and heated at temperatures between 400° and 500° C., stannic oxide is quantitatively transformed into stannic iodide and can thus be completely volatilized. This behavior can be used as the basis of analytical procedures for the separation of stannic oxide from most other metallic oxides likely to be associated with it, since these either are not affected by such treatment or are converted more or less completely into nonvolatile iodides which can be transformed back to oxides. For example, impure ignited tin oxide, such as that resulting from the nitric acid treatment of common non-ferrous alloys, may be corrected for impurities in this way. The experiments show that this method of separation is simple, rapid, and accurate.

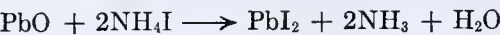
tirely satisfactory, since there is danger of mechanical loss due to the formation of a certain proportion of very light, fluffy ferric oxide. For this reason it is better to treat the iodide with 2 to 3 ml. of nitric acid first, evaporate, then ignite the resulting nitrate to oxide.

The reaction of ammonium iodide with cupric oxide is analogous to that with ferric oxide as indicated by the equation



In this case, however, it is not so convenient to convert the iodide back to oxide by air oxidation, since this takes a longer time and more care than with ferrous iodide. Apparently no loss from volatilization of cuprous iodide occurs if ignitions are made at any temperature in the range 400° to 500° C.

The action of ammonium iodide on lead oxide can be represented by the equation



In this case also the ignition must be made with temperature control to prevent loss by volatilization. Conversion to oxide through nitric acid treatment is necessary for quantitative results since lead iodide is converted into oxyiodides by ignition in air (5). Large amounts of lead oxide, however, cannot be handled conveniently by this method, since then the conversion of the iodide back to oxide was found to require an excessive number of repeated treatments with the acid. With as much as 0.01 to 0.02 gram, far in excess of amounts likely to be found in impure tin oxide precipitates, the recovery is fairly satisfactory.

In the case of nickel oxide the equation representing the reaction is analogous to the one for lead oxide. From a manipulative viewpoint the behavior of nickel oxide is similar to that of ferric oxide, for not only is the conversion of the iodide back to oxide by direct ignition in air possible, but there is also likelihood of the formation of a fluffy form of this oxide which can lead to mechanical loss unless due care is taken.

With zinc oxide the reaction follows a course analogous to that of the last two oxides, but owing to the relatively low boiling point of zinc iodide considerable loss by volatilization occurs when the ignitions are conducted within the temperature range used for the preceding oxides. From the standpoint of the application of this method to the correction of impure tin oxide for impurities, it is fortunate that zinc is such a minor contaminant of such precipitates.

Antimony trioxide on ignition with ammonium iodide behaved in a manner very similar to that of stannic oxide. The equation for the volatilization can be written



Separation of these oxides is therefore not possible by this method. On the contrary the two oxides can be quantitatively volatilized together from mixtures containing other oxides, and this procedure can be applied with advantage in certain cases.

Separation of Stannic Oxide from Other Metallic Oxides

The separation of ferric oxide from stannic oxide is important practically because ferric oxide is often the chief contaminant of impure tin oxide. A number of experiments were, therefore, made on synthetic mixtures in which the weights of the oxides were so taken as to give samples that simulated badly contaminated tin oxide precipitates. In each trial a sample was weighed into a weighed crucible and intimately mixed with 1.5 grams of ammonium iodide. Ignition was performed at various temperatures, and the crucibles with their residues were then gently ignited to constant weight in air to obtain the amounts of residual oxide. Typical

results are shown in Table I. With an ignition temperature below 400° C. high results were obtained by reason of the nonvolatilization of some of the stannic oxide, whereas at 500° C. the results were low because of volatilization of some ferrous iodide during ignition. At the intermediate temperatures, however, the separation is, in general, good. Some experiments were also made on mixtures which had larger proportions of ferric oxide but, the results on these not being as satisfactory, the method is not to be recommended for such separations.

TABLE I. SEPARATION OF STANNIC OXIDE FROM FERRIC OXIDE BY IGNITION WITH AMMONIUM IODIDE

Temperature ° C.	SnO2 Taken Gram	Fe2O3 Taken Gram	Fe2O3 Residue Gram	Difference Error Gram
345	0.0993	0.0115	0.0220	+0.0105
395	0.1151	0.0094	0.0122	+0.0028
420	0.0932	0.0109	0.0106	-0.0003
420	0.0978	0.0112	0.0111	-0.0001
430	0.1027	0.0174	0.0177	+0.0003
430	0.1017	0.0119	0.0116	-0.0003
450	0.0943	0.0125	0.0122	-0.0003
450	0.0958	0.0111	0.0112	+0.0001
450	0.1066	0.0100	0.0101	+0.0001
450	0.0986	0.0100	0.0098	-0.0002
460	0.0983	0.0101	0.0097	-0.0004
460	0.0956	0.0116	0.0115	-0.0001
500	0.0984	0.0125	0.0116	-0.0009
500	0.0965	0.0140	0.0127	-0.0013

In addition to ferric oxide, cupric oxide is a leading contaminant of ignited stannic oxide precipitates. For this reason a number of experiments were made on synthetic mixtures that contained both these oxides in addition to a large relative excess of stannic oxide. These trials were carried out in the same way as the preceding except that the ignitions in air, because of the presence of cuprous iodide in the residues, were controlled as to temperature, the start being made at about 270° C. with a gradual rise to dull red heat. The results appear in Table II.

TABLE II. SEPARATION OF STANNIC OXIDE FROM FERRIC OXIDE AND CUPRIC OXIDE

Temperature ° C.	SnO2 Taken Gram	Fe2O3 Taken Gram	CuO Taken Gram	Total Foreign Oxides Taken Gram	Found Gram	Error Gram
400	0.1081	0.0090	0.0092	0.0182	0.0183	+0.0001
400	0.0988	0.0077	0.0123	0.0200	0.0202	+0.0002
425	0.0954	0.0104	0.0100	0.0204	0.0202	-0.0002
425	0.1036	0.0105	0.0095	0.0200	0.0199	-0.0001
425	0.0993	0.0022	0.0006	0.0028	0.0029	+0.0001
425	0.0992	0.0020	0.0008	0.0028	0.0028	±0.0000
450	0.1021	0.0085	0.0127	0.0212	0.0211	-0.0001
475	0.0918	0.0065	0.0094	0.0159	0.0159	±0.0000
500	0.1074	0.0079	0.0116	0.0195	0.0194	-0.0001
525	0.1074	0.0067	0.0083	0.0150	0.0146	-0.0004
525	0.0934	0.0097	0.0122	0.0219	0.0214	-0.0005

The totals agree satisfactorily except in the case of the runs made at 525° C. where some volatilization of the iodides probably occurred. A similar set of experiments was carried out in which, instead of air ignition, the nitric acid technic was used for the conversion of iodides to oxides. The results of these were in general also satisfactory.

Samples containing ferric oxide, cupric oxide, and lead oxide that were synthetic approximations to ignited tin oxide precipitates likely to be obtained in the analysis of common non-ferrous alloys were also analyzed in this way. In most of these the proportion of total "impurities" was purposely exaggerated in order to test the value of the method for handling grossly contaminated tin oxide. Because of the presence of lead oxide the reconversion back to oxides was made by the nitric acid method in all these trials. The data in Table III show that the recovery of the total added "foreign" oxides from the synthetic mixtures was satisfactory, especially in view of the possibility of the occurrence of cumulative weighing errors in the preparation of complex mixtures of this sort. As could be expected from the results

of the preceding experiments, the least satisfactory results were obtained on samples that were ignited at the lowest and the highest points in the temperature range.

TABLE III. SEPARATION OF STANNIC OXIDE FROM FERRIC OXIDE, CUPRIC OXIDE, AND LEAD OXIDE

Temperature ° C.	SnO ₂ Taken	Fe ₂ O ₃ Taken	CuO Taken	PbO Taken	Total Foreign Oxides Taken	Found	Error
	Gram	Gram	Gram	Gram	Gram	Gram	Gram
400	0.1682	0.0078	0.0096	0.0037	0.0211	0.0214	+0.0003
400	0.1376	0.0011	0.0016	0.0006	0.0033	0.0037	+0.0004
425	0.1101	0.0037	0.0055	0.0028	0.0120	0.0119	-0.0001
450	0.1453	0.0013	0.0008	0.0016	0.0037	0.0040	+0.0003
450	0.1130	0.0049	0.0053	0.0083	0.0185	0.0184	-0.0001
450	0.0959	0.0020	0.0014	0.0011	0.0045	0.0049	+0.0004
450	0.0981	0.0033	0.0076	0.0029	0.0138	0.0136	-0.0002
475	0.0990	0.0046	0.0054	0.0048	0.0148	0.0146	-0.0002
475	0.0978	0.0038	0.0030	0.0041	0.0109	0.0108	-0.0001
500	0.0819	0.0017	0.0011	0.0006	0.0034	0.0034	±0.0000
500	0.0642	0.0056	0.0032	0.0042	0.0130	0.0131	+0.0001
525	0.0875	0.0024	0.0017	0.0024	0.0065	0.0060	-0.0005

Behavior of Difficultly Soluble Oxides

The two oxides of this type considered here differ from the other oxides likely to be contaminants of stannic oxide in their behavior on ignition with ammonium iodide, for no conversion to iodides takes place. In the case of tungstic oxide some slight reduction to a lower oxide apparently occurs if the temperature of ignition is too high, but with silica there is no reaction.

Experiments on mixtures of tungstic oxide and stannic oxide showed that this general method is practicable for the separation of the two. Some results are shown in Table IV.

TABLE IV. SEPARATION OF STANNIC OXIDE FROM TUNGSTIC OXIDE

Temperature ° C.	SnO ₂ Taken	WO ₃ Taken	WO ₃ Residue	Difference Error
° C.	Gram	Gram	Gram	Gram
375	0.1280	0.1129	0.1147	+0.0018
400	0.0113	0.1126	0.1127	+0.0001
400	0.0770	0.0686	0.0685	-0.0001
425	0.0114	0.1634	0.1635	+0.0001
425	0.1164	0.0976	0.0972	-0.0004
450	0.0104	0.1504	0.1502	-0.0002
450	0.0906	0.1085	0.1086	+0.0001
475	0.1510	0.1419	0.1413	-0.0006

In these trials each sample was mixed with about 1.5 grams of ammonium iodide and ignited in the electric furnace at the given temperatures. The residual oxide was then simply weighed after volatilization of all excess iodide. The usual high results that come from incomplete removal of stannic oxide on using too low an ignition temperature are illustrated by the first value. In the remaining trials, with the exception of the last, the residual oxide had a normal appearance, and the separation was satisfactory. In ignitions made above 450° C. the oxide had a slight greenish color apparently due to superficial reduction, and low results were obtained. However, if concentrated nitric acid was added to such a residue and then removed by evaporation, the oxide regained its normal appearance and proper weight. In the separation of stannic oxide from tungstic oxide, therefore, it is best to ignite with ammonium iodide at a temperature between 400° and 450° C., but if too high a temperature happens to be used the residue can be oxidized back with nitric acid.

TABLE V. SEPARATION OF STANNIC OXIDE FROM SILICA

SnO ₂ Taken	SiO ₂ Taken	SiO ₂ Recovered	Difference Error
Gram	Gram	Gram	Gram
0.0923	0.0020	0.0021	+0.0001
0.1197	0.0016	0.0018	+0.0002
0.1930	0.0009	0.0012	+0.0003
0.1230	0.0021	0.0019	-0.0002
0.0992	0.0022	0.0019	-0.0003
0.1196	0.0007	0.0007	±0.0000

In Table V are shown the results of experiments on the separation of stannic oxide from silica.

In order to give a material similar to that likely to be met with in tin oxide precipitates contaminated with silica, that used in these trials was dehydrated silicic acid prepared by ignition, rather than crystalline silica. The samples were mixed with about ten times their weight of ammonium iodide, and the ignitions were conducted over a Bunsen burner at low red heat, no attempt at exact temperature control being made. The separation was satisfactory. For the purpose of correcting the weight of an impure stannic oxide precipitate contaminated with silica it is believed that this ammonium iodide volatilization method is probably more accurate, as well as more convenient, than the usual treatment with hydrofluoric and sulfuric acids, since the new method is conducted in the porcelain crucible used for igniting the oxide, whereas the other method necessitates transference to a platinum vessel. In addition, the process described here is somewhat more rapid.

Application to Determination of Tin in Alloys

It is commonly recognized that the ignited stannic oxide resulting from the nitric acid treatment of such alloys as brasses and bronzes is so contaminated with various impurities that, when exact results are desired, it must be subjected to some purification process. Practically the only method heretofore available for the treatment of such impure tin oxide has been the sodium carbonate and sulfur fusion process of Rose. This method is laborious and time-consuming, especially when a second treatment is required, which is often the case. Furthermore, several sources of error are inherent in it, such as that resulting from the introduction of silica by the action of the fusion mixture on the crucible. Treatment with ammonium iodide volatilizes stannic oxide quantitatively from synthetic mixtures of oxides that resemble in composition the impure tin oxide obtained from ordinary brasses or bronzes, for, if alloys containing arsenic, antimony, or phosphorus are excepted, the usual contaminants of the tin precipitate are ferric oxide, cupric oxide, lead oxide, zinc oxide, and nickel oxide. Actually, according to quantitative data furnished by Hillebrand and Lundell (2), and more extensively by Tilk and Holtje (6), ferric oxide and cupric oxide are the chief impurities, the others being normally present in almost negligible amounts. When applied to the purification of actual precipitates the ammonium iodide volatilization method was found to be very satisfactory. In simplicity and time required it is decidedly superior to the fusion method, and appears to yield more consistent and accurate results. The procedure used in these test analyses and recommended for general use is as follows.

Procedure

Ignite the separated metastannic acid to constant weight in a porcelain crucible. Then add to the impure tin oxide about fifteen times its weight of powdered ammonium iodide, and mix the two in the crucible intimately by means of a small spatula. Place the charged crucible in an electric crucible or muffle furnace maintained between 425° and 475° C. Allow it to remain there until all fumes have ceased to come from the crucible, about 15 minutes. Then remove the crucible and, after having allowed it to cool sufficiently, add 2 to 3 ml. of concentrated nitric acid. Evaporate to dryness on the hot plate and cautiously decompose the residual nitrates over a low burner flame. Follow this by ignition at low red heat to constant weight. The difference between this weight and the original weight gives the amount of pure stannic oxide present. A suitable correction should be applied if there is a weighable amount of nonvolatile matter in the ammonium iodide. To continue the analysis, dissolve the oxide residue out of the crucible by digestion with a few milliliters of hot concentrated hydrochloric acid. Dilute the resulting solution and filter it to remove small amounts of silica that may come from the filter paper ash. Finally add the solution and washings

to the filtrate being evaporated down for the determination of lead as sulfate. The remainder of the analysis is conducted in the usual way.

Results of Test Analyses

Twelve consecutive determinations of the tin content of Bureau of Standards brass sample No. 37b using 5.000-gram samples and several variations in the method of separating the metastannic acid with 1 to 1 nitric acid yielded the following percentage values based upon the weights of the impure tin oxide: 1.09, 1.06, 1.11, 1.08, 1.09, 1.08, 1.07, 1.04, 1.05, 1.06, 1.06, and 1.06. After purification of the precipitates by the above method the corresponding values were 1.00, 0.99, 1.00, 0.98, 0.99, 0.99, 1.00, 0.99, 0.99, 0.97, 0.98, and 0.98, the average being 0.99. Though the percentages of tin based upon the weight of impure oxide show a range of 0.07 per cent, due in part to deliberate variations in the method of treatment in order to introduce varying amounts of impurities, the values after purification show a range of only 0.03 per cent between the extreme results. The value established at the Bureau of Standards on this sample was 1.00 per cent using a volumetric method, while the co-operating analysts obtained by various gravimetric and volumetric procedures the percentages 0.99, 0.98, 0.91, 0.99, 1.01, 0.97, 0.99, 1.02, 0.98, and 1.03, the over-all average of 0.99 per cent being identical with the average of the present determinations.

The above procedure can also be applied to certain alloys that contain a higher percentage of tin, such as ordinary bronzes. It is even applicable to bronzes that contain a small proportion of antimony if the latter is known or determined and allowance is made for the corresponding amount of antimony oxide that is volatilized along with the stannic oxide during the ignition with ammonium iodide. While this method involves the use of a double correction, it apparently yields satisfactory results, as shown by test determinations made on Bureau of Standards cast bronze sample

No. 52. For these 1.0000-gram samples were taken, and for the antimony content the stated average value, 0.16 per cent, was used. Six consecutive determinations gave the following final values for the tin content: 7.85, 7.86, 7.87, 7.85, 7.87, and 7.88, the average being 7.86 per cent. The value established at the Bureau of Standards was 7.88 per cent, while the co-operating analysts obtained percentages ranging from 7.80 to 7.99, the over-all average being 7.90 per cent. In the case of this sample also the results were not only accurate but very consistent, the range between the extreme values of the single determinations being but 0.03 per cent.

Discussion

It is believed that this general method for the separation of stannic oxide represents a distinct advance over methods previously proposed, not only from the standpoint of accuracy, but also in respect to simplicity of manipulation and the rapidity with which results can be obtained. The ammonium iodide volatilization method can be applied to separations and materials other than those considered in this present paper.

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The Ignition of Silicic Acid

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SEVERAL years ago, one of us was disturbed upon being presented with a platinum crucible containing a jet-black substance which was stated to be the product obtained on igniting a sample of silica separated in the course of an ordinary analysis of a silicate. On interrogating the student, it was learned that the moist silicic acid, on a wet filter paper, had been placed in a well-covered crucible and the vessel and contents had been immediately subjected to the highest temperature attainable with a large Meker burner. In the belief that the color was due to carbon, the uncovered crucible and contents were heated for several hours without effecting a detectable change in appearance or in weight. By means of a suitable porcelain cover and inlet tube, oxygen was supplied to the crucible and the contents were heated for a 6-hour period in that atmosphere. The contents were unaltered in appearance and lost but 1.5 mg. in weight. A second and third heating for 6-hour periods produced a total loss of 3 mg. in weight. The color changed from black to dark gray.

These observations suggested to the writers that some compound of silicon might be responsible for the observed resistance to oxidation, although no reference to compound formation under these conditions could be found in the literature. To test this supposition, silica was precipitated from solutions of sodium silicate by the addition of hydrochloric acid, washed repeatedly by stirring and decantation to remove sodium

chloride, and collected on quantitative filter paper (Whatman No. 42, 7 cm.). Samples, while wet, were put in covered crucibles of platinum and of sillimanite, and immediately placed over Meker burners. Provided the silica and filter paper were wet and the crucibles covered, the ignition product was invariably dark in color. On treating the product with hydrofluoric acid and evaporating to dryness, a black powder was obtained which always left a small, black residue when ignited in the air. On examination under the polarizing microscope, this residue was found to be silicon carbide, SiC. A few imperfect, greenish blue crystals were found in one sample, which gave evidence of the characteristic pleochroism. The index of refraction of this substance was found to be higher than that of methylene iodide ($N = 1.74$), thus definitely excluding the possibility that the substance was merely silica mechanically darkened by carbon.

It is presumed that the carbide is produced by the action of the carbon, hydrocarbons or carbon monoxide, and hydrogen resulting from the ignition of the wet filter paper, although the temperature attained in a 20-cc. platinum crucible, when heated under the conditions of the experiments, was never higher than 930° to 950° C., as determined by means of a platinum-platinum rhodium thermocouple.

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Determining Copper in the Presence of Interfering Elements

A Modified Iodometric Method

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THE usual iodometric method of determining copper consists essentially of adding a soluble iodide to a solution of a cupric salt and titrating the liberated iodine with standard thiosulfate. In a recent article (1) the writers have shown that, if a soluble thiocyanate is added to the solution just before the end point is reached, some additional iodine is liberated and the reaction runs to completion in stoichiometric proportions. The end point is extremely sharp, partly because of the greater insolubility of cuprous thiocyanate and partly because the precipitate is white and retains no adsorbed iodine.

The present article gives the results obtained by using this modified method to determine copper in the presence of pentavalent arsenic and antimony, and ferric iron. These are the only elements commonly associated with copper which liberate iodine from iodides and thus make the titration unreliable. All these elements, in their lower valences, can reduce iodine and in that way also lead to incorrect results. It is, however, a simple matter to insure the presence of the higher valence only, so that this latter type of interference need not occur. The possible interference of selenium and manganese has also been considered.

The interference of pentavalent arsenic (arsenic acid) and ferric iron in the usual iodometric method for copper has been investigated recently by Park (3) who found that arsenic acid offered the chief difficulty. On account of its oxidizing character in the presence of mineral acids, he found it necessary to reduce the hydrogen-ion concentration by means of buffer solutions, but encountered the difficulty, which was not new, that the liberation of iodine by the cupric salt was excessively slow at the low acidity. He abandoned the use of acetates for this reason and used a buffered phthalic acid solution. To what extent the reaction runs in stoichiometric proportions under these conditions is not clear, as he standardized his thiosulfate with copper. Park found, in accordance with Mott (2) and others, that a soluble fluoride eliminated all difficulty with the iron. The latter is converted to a complex fluoride insufficiently dissociated to liberate iodine from potassium iodide.

Experimental

Metallic copper was from the sample used in the previous investigation (1), and contained 99.955 per cent of copper. Arsenic was used in the form of H_2KAsO_4 , and antimony as a potassium antimonate containing 46.5 per cent of the metal. A standardized solution of ferric nitrate furnished the iron. Thiosulfate solutions were standardized by means of resublimed iodine and the copper equivalent was calculated. While equally good or better results could be obtained by standardizing with copper, the authors considered it essential to use iodine as a standard in order to determine to what extent the reaction $2\text{CuI}_2 \rightleftharpoons 2\text{CuI} + \text{I}_2$ runs to completion during the titration. The thiosulfate solutions changed slightly in strength during the work and were frequently restandardized.

In preliminary experiments the authors determined empirical proportions of sulfuric and acetic acids and ammonia which would yield a buffer solution of sufficiently high pH to

prevent the oxidation of an iodide to free iodine by arsenic acid. The buffer solution adopted contained the equivalent of 9.3 cc. of 6 *N* sulfuric acid, 22.8 cc. of 6 *N* acetic acid, and 12.6 cc. of 6 *N* ammonia. This mixture in a total volume of 60 cc. has a pH value approximating 3.7 as determined by the hydrogen electrode. These proportions were used in all determinations given below. An acetate solution of this pH practically cannot be used in the usual iodometric determination of copper. In the presence of a thiocyanate, however, the reaction is rapid and the end point exceedingly sharp.

In all determinations given below the following procedure was used:

Known weights of copper were dissolved in nitric acid and 9.3 cc. of 6 *N* sulfuric acid, together with the interfering elements, added to the solution. The solution was then evaporated until all nitric acid was removed. After evaporation the residues were dissolved in 20 cc. of water and the acetic acid and ammonia added in the volumes noted above; the acetic acid was added first so that the solution was always acid. When iron was present the solution was deeply colored at this point. A basic precipitate containing iron may form, particularly if arsenic is present. One to two grams of sodium fluoride were next added, if iron were present, which immediately removed all color of iron and dissolved any precipitate. Usually a slight, apparently crystalline precipitate appeared at this point (Na_3FeF_6 ?) which, however, in no way interfered with the titration. After adding potassium iodide, the titration was carried out until most of the iodine was removed, then starch solution was added and, when the end point was nearly reached, 2 to 3 grams of ammonium thiocyanate, and the titration was completed.

Certain details of the above procedure require mention.

1. The complete removal of nitric acid was found to be necessary, not because nitric acid itself interferes in the titration, but because it appears to break down as the last of it is removed by evaporation from the strong sulfuric acid and the resulting nitrogen oxides liberate iodine later in the analysis. Blank tests in the absence of copper showed this conclusively and determinations of copper, in which the nitric acid was purposely not removed entirely, gave high results. The nitric acid can be removed conveniently either by evaporating until the sulfuric acid fumes strongly, or by carrying out the first evaporation until salts begin to crystallize and evaporating a second time after adding a small volume of hydrochloric acid. Both methods were used indiscriminately. Where there is difficulty with spattering, the second method is more convenient.

2. All evaporations were made by boiling the solutions, usually in 300-cc. flasks, over a free flame, holding the flasks nearly horizontal. To show that losses from this treatment were negligible, two solutions containing known amounts of copper were evaporated repeatedly in the manner described, adding 20 cc. of liquid to the residue after each evaporation. The loss in copper after ten such evaporations was less than could be detected by analysis.

3. The amount of sulfuric acid used can be varied, but there should be a corresponding variation in the amount of ammonia. The authors chose to use 10 rather than 5 cc. (used in the previous work) because evaporation and subsequent solution in water are a little easier, particularly in the presence of rather large amounts of salts.

TABLE I. DETERMINATION OF COPPER IN ABSENCE OF INTERFERING ELEMENTS

(1 to 7, volume buret used; 8 to 17, weight buret used)			
No.	Pure Cu Taken	Cu Found	Error
	Gram	Gram	Mg.
1	0.1641	0.1641	0
2	0.1971	0.1970	-0.1
3	0.3208	0.3211	+0.3
4	0.1592	0.1591	-0.1
5	0.2198	0.2197	-0.1
6	0.1784	0.1785	+0.1
7	0.3034	0.3034	0
8	0.1529	0.1532	+0.3
9	0.2028	0.2031	+0.3
10	0.2585	0.2586	+0.1
11	0.3028	0.3033	+0.5
12	0.3543	0.3547	+0.4
13	0.1559	0.1558	-0.1
14	0.2008	0.2011	+0.3
15	0.2509	0.2511	+0.2
16	0.3027	0.3030	+0.3
17	0.3570	0.3575	+0.5

TABLE II. DETERMINATION OF COPPER IN PRESENCE OF TRIVALENT IRON

(1 to 8, volume buret; 9 to 18, weight buret)				
No.	Fe	Pure Cu Taken	Cu Found	Error
	Gram	Gram	Gram	Mg.
1	0.069	0.1536	0.1536	0
2	0.069	0.1785	0.1787	+0.2
3	0.069	0.2149	0.2149	0
4	0.069	0.3031	0.3033	+0.2
5	0.138	0.1595	0.1597	+0.2
6	0.138	0.1918	0.1918	0
7	0.069	0.2294	0.2293	+0.1
8	0.069	0.3076	0.3078	+0.2
9	0.069	0.1546	0.1546	0
10	0.069	0.2015	0.2017	+0.2
11	0.069	0.2548	0.2548	0
12	0.069	0.3027	0.3029	+0.2
13	0.069	0.3542	0.3545	+0.3
14	0.138	0.1525	0.1527	+0.2
15	0.207	0.2032	0.2031	-0.1
16	0.104	0.2744	0.2747	+0.3
17	0.138	0.3354	0.3359	+0.5
18	0.138	0.4021	0.4028	+0.7

TABLE III. DETERMINATION OF COPPER IN PRESENCE OF PENTAVALENT ARSENIC

(1 to 8, volume buret; 9 to 17, weight buret)				
No.	As	Pure Cu Taken	Cu Found	Error
	Gram	Gram	Gram	Mg.
1	0.125	0.1637	0.1639	+0.2
2	0.08	0.2138	0.2138	0
3	0.08	0.2100	0.2103	+0.3
4	0.17	0.3090	0.3092	+0.2
5	0.04	0.1788	0.1789	+0.1
6	0.08	0.2098	0.2100	+0.2
7	0.125	0.2385	0.2387	+0.2
8	0.17	0.3040	0.3042	+0.2
9	0.04	0.1033	0.1034	+0.1
10	0.08	0.1501	0.1504	+0.3
11	0.126	0.2041	0.2047	+0.6
12	0.21	0.3024	0.3023	-0.1
13	0.25	0.3502	0.3504	+0.2
14	0.29	0.4019	0.4023	+0.4
15	0.33	0.4412	0.4422	+1.0
16	0.125	0.1547	0.1549	+0.2
17	0.33	0.3004	0.3004	0

4. In adding acetic acid and ammonia it was found best to add them in the order mentioned, so that the solution never became basic. If the reverse order is used, the precipitate produced by ammonia is somewhat difficult to dissolve. Further, in the presence of manganese, it is essential to add the acetic acid first, as will be shown later.

5. The addition of sodium fluoride is, of course, necessary only when iron is present. It not only prevents the ferric iron from liberating iodine when potassium iodide is added, but it also completely prevents the ferric thiocyanate color when a thiocyanate is added near the end point. One gram of sodium fluoride is sufficient for somewhat more than 0.1 gram of iron.

6. Roughly, half the determinations were made with a calibrated volume buret and the others with a weight buret. With the latter, somewhat larger amounts of copper could be determined, but the percentage error by the two methods was nearly the same.

Determination of Copper Alone and in the Presence of Iron and Arsenic

The results obtained on copper alone are given in Table I. This series of determinations was carried out in order to show definitely that the method was reliable at the rather high pH necessary to prevent the oxidation of iodides by arsenic acid. The highest pH of the solutions in the authors' previous work was approximately 2.0, and iodides are oxidized freely by arsenic acid at that hydrogen-ion concentration. Tables II, III, and IV give the results on copper in the presence of iron, of arsenic, and of both iron and arsenic, respectively.

Tables II, III, and IV show that neither iron nor arsenic when present alone interferes with the copper determination under the conditions used even though either may be present in fairly large amounts; further, when iron and arsenic are present together, they do not interfere when present in moderate amounts. Although the amounts of iron and arsenic shown in Table IV are in excess of the amounts likely to be encountered in copper ores, it seemed of interest to find the quantities of these two elements which would limit the applicability of the method when they were both present. Table V gives these results.

The results are low, owing to the formation of a precipitate, presumably an iron arsenate, which contains some copper. No entirely definite line can be drawn between amounts which do and which do not vitiate the method, but a rather close idea can be obtained from the values in Tables IV and V. The use of a larger volume of solution did not solve the difficulty. If, in practice, such excessive amounts of iron and arsenic were found, it might well be possible to avoid the difficulty by using a smaller sample of material.

Determination of Copper in the Presence of Antimony

Pentavalent antimony in solution behaves very similarly to pentavalent arsenic as an oxidizing agent. At the pH used in all the authors' determinations it liberates iodine only in traces with extreme slowness and offers no difficulty on this account. Antimonic acid, however, is rather insoluble under

TABLE IV. DETERMINATION OF COPPER IN PRESENCE OF TRIVALENT IRON AND PENTAVALENT ARSENIC

(1 to 7, volume buret; 8 to 9, weight buret)					
No.	Fe	As	Pure Cu Taken	Cu Found	Error
	Gram	Gram	Gram	Gram	Mg.
1	0.069	0.04	0.2072	0.2071	-0.1
2	0.069	0.08	0.1623	0.1619	-0.4
3	0.035	0.17	0.3006	0.3007	+0.1
4	0.069	0.17	0.1571	0.1571	0
5	0.069	0.125	0.2316	0.2314	-0.2
6	0.035	0.08	0.1887	0.1892	+0.5
7	0.139	0.04	0.3029	0.3032	+0.3
8	0.069	0.04	0.3016	0.3016	0
9	0.069	0.04	0.3036	0.3038	+0.2

TABLE V. DETERMINATION OF COPPER IN PRESENCE OF LARGER AMOUNTS OF BOTH TRIVALENT IRON AND PENTAVALENT ARSENIC

(Weight buret used)					
No.	Fe	As	Pure Cu Taken	Cu Found	Error
	Gram	Gram	Gram	Gram	Mg.
1	0.035	0.21	0.3020	0.3015	-0.5
2	0.207	0.21	0.3005	0.2999	-0.6
3	0.138	0.29	0.1512	0.1509	-0.3
4	0.069	0.21	0.1496	0.1492	-0.4
5	0.069	0.21	0.4522	0.4515	-0.7
6	0.069	0.42	0.3010	0.3000	-1.0
7	0.069	0.29	0.3002	0.2989	-1.3
8	0.069	0.42	0.3017	0.3004	-1.3
9	0.069	0.42	0.3035	0.3023	-1.2
10	0.069	0.42	0.3028	0.3012	-1.6
11	0.207	0.29	0.3026	0.3009	-1.7
12	0.138	0.29	0.4541	0.4510	-3.1

the conditions necessary for the titration and when it precipitates it always adsorbs small amounts of copper. This behavior is very similar to that of metastannic acid. Whenever antimony is present in considerable amounts, therefore, the results are low. Table VI gives these results. Roughly, the limit of solubility of antimonious acid in the solution used corresponds to 0.020 gram of antimony and this value thus gives the limiting amount of antimony which will cause no difficulty in the titration.

TABLE VI. DETERMINATION OF COPPER IN PRESENCE OF PENTAVALENT ANTIMONY

(1 to 3 and 6, volume buret; 4, 5, and 7, weight buret)				
No.	Sb Gram	Pure Cu Taken Gram	Cu Found Gram	Error Mg.
1	0.005	0.1569	0.1564	-0.5
2	0.005	0.2111	0.2112	+0.1
3	0.005	0.1792	0.1792	0
4	0.009	0.2039	0.2039	0
5	0.019	0.2044	0.2045	+0.1
6	0.024	0.3042	0.3029	-1.3
7	0.038	0.2037	0.2020	-1.7

Determination of Copper in the Presence of Selenium

Selenic acid is a strong oxidizing agent, and would, if present, liberate iodine. Under the conditions of the analysis, however, the element appears to be oxidized only to selenious acid and does not interfere. The results obtained are given in Table VII.

TABLE VII. DETERMINATION OF COPPER IN PRESENCE OF SELENIUM

(Weight buret used)			
Se Gram	Pure Cu Taken Gram	Cu Found Gram	Error Mg.
0.005	0.2013	0.2013	0
0.0505	0.2020	0.2018	-0.2

Determination of Copper in the Presence of Iron and Manganese

The need to determine copper in the presence of appreciable amounts of iron and manganese is rare and the authors would not have considered the matter except that Park (3) states that in the presence of both these metals the results on copper are high, and gives data to show this effect. Disregarding his explanation, it seemed probable that the difficulty was due to the fact that in preparing his buffer solutions, Park made them ammoniacal before acidifying with phthalic acid, and manganous hydroxide, as is well known, forms a higher oxide rather rapidly when exposed to air. This, of course, would liberate iodine later in the analysis. The authors therefore carried out a number of determinations in the presence of manganese alone and in the presence of manganese and iron. The results are given in Table VIII.

TABLE VIII. POSSIBLE EFFECT OF MANGANESE ON DETERMINATION OF COPPER

(All the determinations were carried through as usual except that in Nos. 1 and 2 the ammonia was added before the acetic acid and the ammoniacal solutions allowed to stand 5 minutes before acidifying.)

No.	Pure Cu Gram	MnSO ₄ Gram	Fe Gram	Cu Equivalent of Iodine Liberated
1	None	0.55	None	0.0029
2	None	0.55	0.138	0.0075
3	None	0.55	None	None
4	None	0.55	0.138	None
5	0.2111	0.55	0.138	0.2106
6	0.1838	0.28	0.069	0.1837

Nos. 1 and 2 in Table VIII show the considerable effect due to manganese alone or in the presence of iron, when the solutions were allowed to become alkaline. Both effects are

greater than those obtained by Park, probably because the solutions were purposely allowed to stand, while ammoniacal, for some time in order to intensify the effect. Apparently the presence of iron hydroxide catalyzes the oxidation of the manganese, which accounts for the fact that Park found the effect of manganese appreciable only in the presence of iron. Nos. 3 to 6 show that manganese and iron do not affect the results if the solution is not allowed to become ammoniacal.

Summary

By using a modified iodometric method described recently, and controlling the hydrogen-ion concentration, copper may be determined accurately in the presence of pentavalent antimony and arsenic. The addition of a soluble fluoride (as first suggested by Mott) prevents the interference of iron and does not interfere with the accuracy of the determination. These are the only elements commonly associated with copper which interfere in the usual iodometric determination. Selenium does not interfere under the conditions used. An explanation of the reported interference of a mixture of manganese and iron has been found. Under suitable conditions, these elements do not interfere.

The method is reliable in the presence of rather excessive amounts of arsenic and iron. In the presence of antimony in amounts greater than about 20 mg. antimonious acid precipitates together with adsorbed copper and the results are correspondingly low.

The liberation of iodine from a soluble iodide by cupric copper takes place in stoichiometric proportions under the conditions used.

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(2) Mott, W. R., *Chemist-Analyst*, No. 5, 7 (1912).
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RECEIVED October 2, 1935.

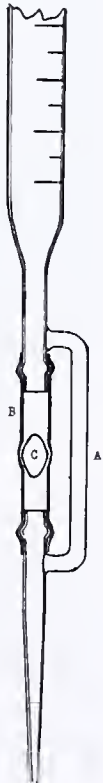
A New Buret for Alkali Titrations

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ALTHOUGH the ordinary rubber-tipped buret has long been recognized as not being strictly accurate for alkaline titration, it still finds wide use in many laboratories. One of the main objections to rubber-tipped burets is their lack of rigidity. The modification presented herewith provides a means whereby this difficulty is overcome and at the same time improves its usefulness. The new type of buret has been tried out by several individuals and all endorse it heartily.

The construction may be seen from the figure. A is a glass rod or sealed-off tube which fastens the tip rigidly in line with the main body of the buret. B is a short piece of a good grade of laboratory rubber tubing connecting the buret to the tip. C as shown in the diagram is a glass bead, but obviously it could be replaced by any of the various devices used in conjunction with rubber stopcocks.



RECEIVED December 31, 1935.

Semi-Micromethod of Analysis for Nitrogen

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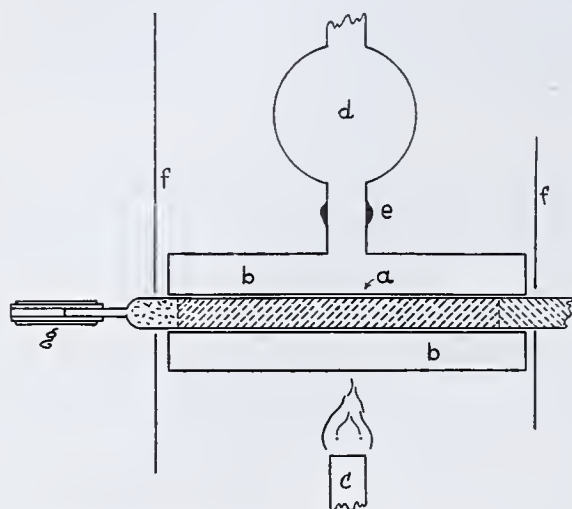


FIGURE 1. DIAGRAM OF APPARATUS

THE Dumas method for nitrogen (3) suffers from two important drawbacks: (1) the copper spiral placed at the end of the combustion tube catalytically reduces the carbon dioxide to carbon monoxide, and (2) this and the intermediate products of combustion are often incompletely oxidized unless the burning produces not more than two bubbles per 3 seconds.

The semi-micromethod described here avoids both difficulties by placing at the end of the tube a heated section containing iodine pentoxide, made by heating iodic acid in an oil bath for an hour at 170° C. At this temperature a minute amount of iodine pentoxide is decomposed, so small, however, that it may be neglected.

A section of the crushed oxide 13 cm. long, *a*, is placed in a combustion tube 56 cm. long and 1 cm. in diameter (Figure 1). The section is kept dehydrated by enclosing it in a copper jacket, *b*, containing boiling xylene (*b. p.* about 120° C. at Boulder, Colo., about 130° C. at 760 mm.). Since this temperature even in high altitudes is well above the melting point of iodic acid (110° C.), the iodine pentoxide is kept sufficiently dehydrated and active. The xylene is heated by burner *c*. Following this are a section of cupric oxide 5 cm. long and a section of reduced copper 5 cm. long. This is followed by a section of cupric oxide 15 cm. long, kept permanently in place by a small roll of copper gauze. The Pyrex condenser, *d*, should have at least four bulbs, each of about 150-cc. capacity to avoid danger from fire, and is sealed to the copper jacket with cementite, *e*. The asbestos screens, *f*, prevent heating of the nitrometer. The combustion tube is connected to the nitrometer by means of a rubber stopper, *g*, which is covered with a short piece of glass tubing to prevent diffusion of air into the apparatus. The combustion stand and set-up are similar to that of Pregl (3).

The sample, 12 to 20 mg., weighed to 0.01 mg. on an analytical balance (5 to 10 minutes), should yield about 1.0 to 2 cc. of nitrogen, and is prepared for analysis as described by Pregl. After the combustion tube is connected to the nitrometer and carbon dioxide generator, the stopcocks are opened and the tube is scrubbed free of air. While the air is being removed, the burner, *c*, is lighted and the xylene brought to boiling as soon as possible. The flame is then lowered so that only gentle boiling occurs during the entire analysis. When the tube is free from air, the nitrometer is filled with potassium hydroxide and the combustion performed in the usual manner. The rate of burning may be such that as many as three to four bubbles of gas per second rise in the nitrometer, but a much faster rate for a few seconds does not endanger the result. The time required for burning the sample is usually about 30 to 45 minutes. The complete determination from the time of weighing of the sample until the results are obtained usually requires an hour.

With a freshly filled tube high results are obtained for the first 7 or 8 analyses, because traces of oxygen are generated by the iodine pentoxide. This may be removed from the gas by washing with a little pyrogallol-potassium hydroxide solution through funnel *e* (Figure 2). The only other difficulty encountered in a series of over two hundred analyses was the rare case where methane, a difficultly combustible gas, was generated as one of the products of decomposition of the burn-



FIGURE 3. MERCURY VALVE

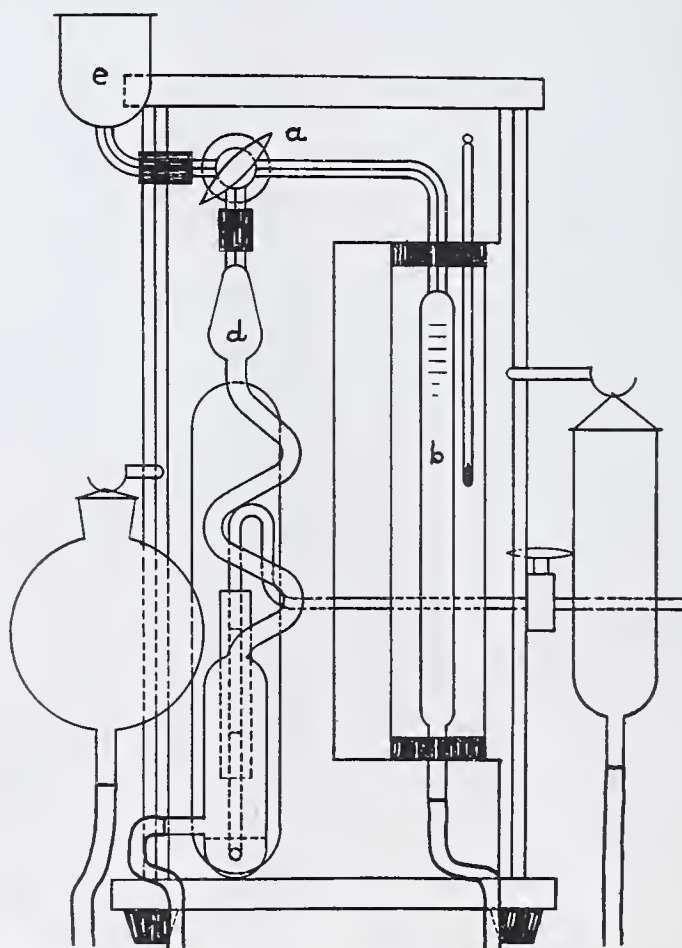


FIGURE 2. MODIFIED NITROMETER

ing compound and was not completely burned (1). In this case there was no decrease in volume after washing the gas first with pyrogallol-potassium hydroxide solution, and then with ammoniacal cuprous chloride solution.

With careful work analyses do not vary more than ± 0.05 per cent.

A modified nitrometer devised for use with this apparatus (Figure 2) consists of an absorption tube connected by means of a three-way stopcock to a gas buret surrounded by a water jacket. The stopcock, *a*, is a capillary three-way stopcock of bore not exceeding 1.5 mm. The gas buret, *b*, is graduated in 0.05 cc. and can be read accurately to 0.01 cc.

When the combustion is finished the gas collected in the absorption buret, *d*, is transferred into the buret, *b*, and the volume read in the usual manner.

The mercuric iodide which forms in the nitrometer inlet

should be removed after about 40 combustions. It is advisable to treat all rubber tubing by Pregl's method to prevent diffusion of gases. Figure 3 shows a diagram of a mercury valve which replaces the one used by Hein in his Kipp generator (2). It is simpler and the materials for making it are more easily available.

Summary

The advantages of the semi-micromethod for nitrogen are: an ordinary analytical balance is used; the sample may usually be burned in the same length of time as that required for the microsample; using the modified nitrometer, the volume of nitrogen may be read in 2 minutes; a sudden increase

in the evolution of gas above the normal rate for a few seconds has no effect on the result; and special training is not necessary for accurate work.

A simple and easily made valve for the Kipp generator is illustrated.

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- (2) Hein, *Z. angew. Chem.*, 40, 864 (1927).
- (3) Pregl, "Quantitative Organic Microanalysis," 2nd ed., pp. 81-4, 90, 94-5, Philadelphia, P. Blakiston's Son & Co., 1930.

RECEIVED June 4, 1935.

Studying the Hardness of Butter Fat

Apparatus and Routine Procedure

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IN A STUDY of factors which influence the physical properties of butter fat there was need for an inexpensive piece of apparatus which would measure accurately the relative hardness of different samples of butter fat. Available pieces of apparatus designed to measure the hardness of materials of similar consistency were not found applicable for various reasons, chief among which were lack of precision and inconvenience of operation within a small constant-temperature chamber. Perkins (2) in discussing several types of apparatus used in studies of fat hardness points out the inadequacies of each and describes a device which determines hardness by the depth of penetration into the fat of standard-size needles falling through a given distance. Apparatus based on this principle require relatively large samples of fat and the application of different weights, depending on the hardness of the fat and the diameter of the needle employed. Coulter and Hill (1) studied butter hardness with a modified apparatus designed to measure the body of cheese.

It was desired to determine the hardness of butter fat at ordinary temperatures with an apparatus which would operate within a constant-temperature water bath and give dependable results over a wide range of values. After building and testing several pieces of apparatus to determine hardness by the depth of penetration of needles of different sizes, by the weight required to crush or force plungers through a given amount of fat, and by a determination of the time required for plungers to sink a given distance into fat, the device here described was found most satisfactory. With this device, hardness is expressed as grams of mercury required to force a plunger 5 mm. in diameter through a disk of butter fat 6 mm. in thickness at 20° C.

The fat disks are made in a two-piece mold which is thoroughly chilled by placing it on the metal divisions of a tray of ice cubes. The base of the mold is a brass plate commonly used in histological technic for paraffin imbedding. A lead ring 4 cm. in diameter and exactly 6 mm. high forms the side of the mold. The melted fat, after thorough mixing at 50° C., is slowly poured into the mold and allowed to cool. A small label bearing the number of the sample is inserted at the edge of the sample for the purpose of identification. When thoroughly hardened, the top of the sample is leveled off even with the top edge of the mold with a straight-edged knife. The whole thing is then placed in ice water and after removing the base of the mold the fat disk is forced out of the ring with very slight pressure. A thin sheet of paper moistened and pressed firmly against the base of the mold to remove air bubbles may be used to prevent the sample of fat from sticking to the base as it hardens. Usually 2 or 3

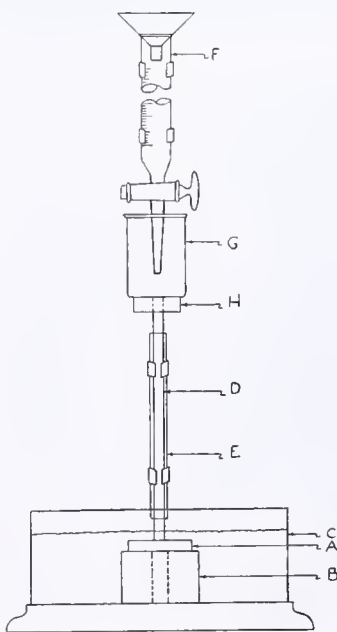
disks are prepared from each sample of fat and kept in ice water overnight or longer. Before the disks are ready for hardness determinations they must be kept for an arbitrarily chosen length of time at the temperature at which the determination is to be made.

Preliminary investigations revealed that the disks soften rapidly during the first 3 or 4 hours when taken from the ice-water bath and placed in the 20° C. bath. After 6 hours very little change in hardness takes place. Since 20° C. has been chosen as the optimal temperature for making these determinations, the disks are kept in a constant-temperature bath held at 20° ± 0.2° C. for 8 hours previous to performing the test. Above 20° C., soft samples of butter fat are difficult to handle; at lower temperatures hard samples tend to crack during the determinations.

The hardness determinations are made with the apparatus sketched herewith.

The fat disk, *A*, 6 mm. thick, is placed over the 9-mm. hole of the cork, *B*, which is cemented to the bottom of the water bath, *C*. The glass rod, *D*, 5 mm. in diameter working in the glass sleeve, *E*, is brought to rest on the disk. The plunger is 19 mm. in length and together with the mercury receptacle, *G*, and its support, *H*, weighs 50.0 grams. Mercury from the 25-cc. buret, *F*, is now run into the 50-cc. beaker, *G*, at a constant rate of 10 cc. per minute. The tip of the buret is approximately 1 cm. above the bottom of the beaker. The flow of mercury is stopped when its weight becomes sufficient to force the plunger through the disk of fat. When this occurs the rubber support, *H*, comes to rest with a sudden thump on the top of the sleeve, *E*. The volume of mercury is determined from the buret readings and its weight calculated.

The entire apparatus can be made of ordinary laboratory equipment. There are no mechanical parts to require special attention or repair. Constant temperatures are easily maintained with two water baths, one at the temperature of a mixture of ice and water and the other close



to room temperature. Hardness is determined at the most desirable temperature from the consumer's standpoint. Only small samples of butter are required for a determination and the number of determinations which can be made with one disk is limited only by the size of the disk. The disks may be remelted and used several times if necessary. Four determinations are usually made with a 4-cm. disk.

TABLE I. HARDNESS OF BUTTER FAT AT TEMPERATURES BETWEEN 18° AND 23° C.

(Hardness is expressed as grams of mercury required to force a plunger measuring 5 mm. in diameter and weighing 50.0 grams through a disk of butter fat 6 mm. in thickness at the temperatures indicated.)

Sample	18.0°	18.6°	19.2°	20.0°	20.6°	21.4°	22.0°	23.0°
1	343	267	206	136	95	51
2	261	216	171	111	70	30
3	270	216	175	127	91	47
4	247	193	148	99	67	34
Cottonseed-Meal Butter Fat								
1	387	309	248	180	139	90
2	412	320	263	193	148	100
3	383	304	242	173	131	80
4	370	289	229	158	112	63

The following buret readings are typical for a series of determinations made on a sample of butter fat at 20° C.: 9.7, 9.2, 10.1, 10, 9.2, 9.0.

The results of hardness determinations performed at temperatures between 18° and 23° C., on four samples of butter fat produced by cows on standard herd rations and four samples produced by cows on heavy cottonseed-meal rations are given in Table I, and emphasize the importance of accurate temperature control. Furthermore they reveal marked differences in the two types of butter fat; differences which are less apparent in the usual fat-constants. The melting points of the herd butter-fat samples were only 3° or 4° lower than those of the cottonseed-meal butter fat, and differences in the iodine numbers were of the same magnitude.

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RECEIVED October 14, 1935.

Determination of Iron by Titanium Titration and by α, α' -Bipyridine Colorimetry

Improved Analytical Procedure

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SINCE Knecht and Hibbert (4) published their monograph on titanous chloride, an increasing number of biochemists have employed this reagent in various reduction processes. It has been used particularly for the estimation of ferric and ferrous iron in biological materials. This involves a microtechnic using very dilute titanium solutions (5). It therefore becomes increasingly difficult to maintain the reducing agent at constant strength for a reasonable period. In general the reagent has been stored under hydrogen and the titration carried out with apparatus of the type designed by Knecht and Hibbert. Satisfactory results are obtained only when the greatest care is taken in purifying the hydrogen and in sealing the apparatus. The necessity for such extreme precautions has deterred the more general application of this valuable reducing agent and has caused many workers to avoid this method for estimating iron and to turn to colorimetric procedures.

Horizontal Microburet

The buret described below was designed to obviate these difficulties and has the following advantages:

1. It is essentially a modification of the Conway buret (2) and retains its excellent features of accuracy in delivering small volumes, simplicity of construction, and ease of calibration.
2. The titrating reagent comes into contact only with mercury. Under these conditions the author has found that the titer of the reagent against a standard ferric chloride solution remains practically unchanged over a period of at least 4 months.
3. Expelling the fluid from the buret by a mercury column gets rid of a common difficulty in the use of titanium solutions, that of sticking in the buret, and makes cleaning unnecessary.
4. Recharging the buret is extremely simple.
5. A large number of titrations may be made without refilling.

CONSTRUCTION. The apparatus (Figure 1) is constructed of soft glass and mounted on a 3-ply board (87 × 48 cm.). Capillary tubing of approximately 1-mm. bore is used for the buret, *f*, *e*. The buret proper, *f*, is 67 cm. long and is backed by a strip of graph paper, ten squares to the inch and 25 inches in

length. At the left end it is connected by pressure tubing to a small (2 × 5 cm.) mercury reservoir, *d*, and at the right end it is connected by a ground-glass joint to a three-way stopcock, *e*. The mercury reservoir, *d*, is adjustable to a height of 3 cm. above and below the level of tube *f* by means of the rack and pinion, *g*. The buret is connected by a second ground-glass joint to the reagent storage vessel, *a*, which has a capacity of 200 cc. and which in turn is connected by pressure tubing to a leveling bulb, *b*, of approximately the same capacity. The storage flask is painted with two coats of black enamel and set into the board by cutting out a strip. The delivery tube, supported by a bracket (13 × 13 cm.), is drawn out to a fine capillary, the tip of which has a clearance of 16 cm. from the base board (28 × 87 cm.).

The two ground-glass connecting pieces are used to facilitate assembling the apparatus. These unfortunately had hollow bulbs which the author anticipated would be difficult to fill with liquid and which might cause the liquid column to break. A continuous capillary joint was obtained by filling the bulbs (*a*, Figure 2) with sealing wax as follows:

A piece of copper wire of slightly larger diameter than the capillary bore was well smeared with vaseline and inserted through *c* to plug the capillary at *b*. The copper wire was then packed around, and bulb *a* completely filled with finely powdered sealing wax. By gentle heating the sealing wax was melted. The coating of vaseline made possible the withdrawal of the copper wire after the wax had solidified. The surface of the wax was ground with a small carpenter's bit so that the connecting piece, *d*, fit snugly.

CALIBRATION. This was carried out with titanous chloride solution and checked with mercury, weighing in each case the total of five deliveries of the graduated section. The entire graduated portion (250 divisions) had a volume of 0.718 cc.

PREPARATION OF TITANOUS CHLORIDE SOLUTION. Preliminary tests indicated that the most satisfactory thiocyanate end point could be obtained when the strength of the reducing agent was such that approximately 0.25 cc. (87 buret divisions) of the titanous chloride solution just effected the com-

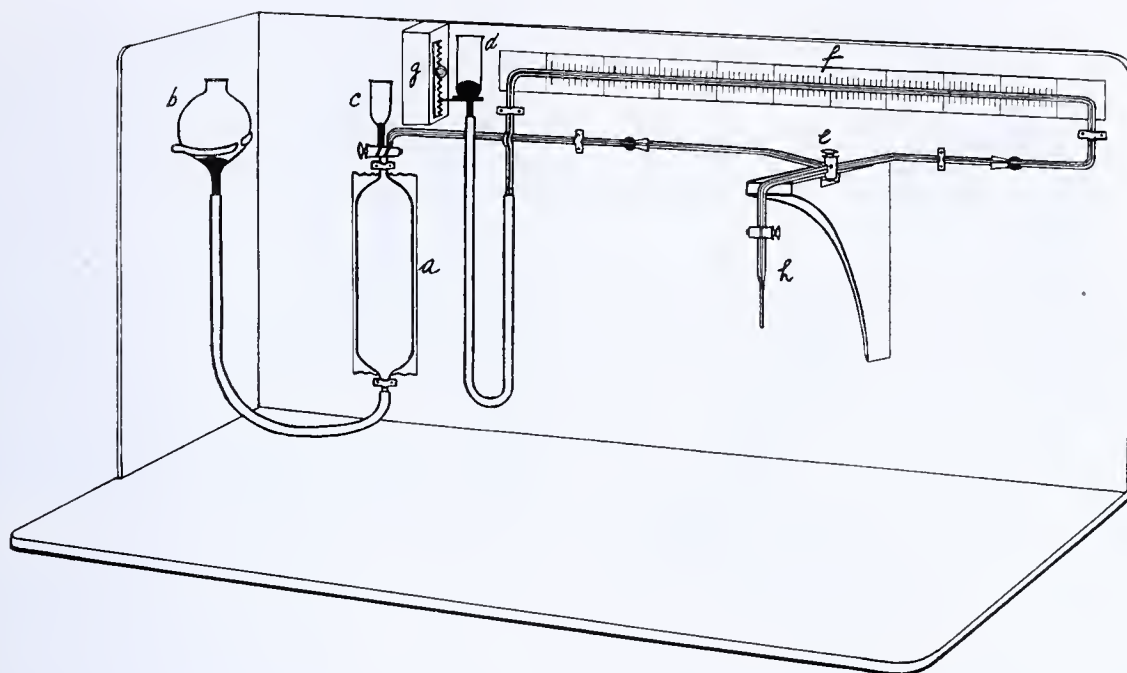


FIGURE 1. DIAGRAM OF APPARATUS

plete reduction of 0.05 mg. of Fe^{+++} in a total volume of 20 cc. An approximately 0.004 *N* titanous chloride solution was prepared as follows:

To 200 cc. of boiling *N* hydrochloric acid a 20 per cent titanous chloride solution was added, so that 0.25 cc. of the mixture just discharges the red color of 10 cc. of a ferric thiocyanate solution containing 0.05 mg. of Fe^{+++} . About 0.3 cc. of the 20 per cent titanous chloride solution is required.

CHARGING THE APPARATUS. The entire apparatus is first filled with mercury. The titanous chloride solution is quickly cooled and transferred to the storage vessel, *a*, through inlet *c* with the mercury level, *b*, lowered. Inlet *c* is sealed with a few drops of mercury. The mercury reservoir, *b*, is returned to its support which is high enough to give a slight positive pressure to the buret side of the apparatus. The stopcock of the storage vessel is turned to join *a* and *c* and by manipulating the three-way stopcock, *e*, with the mercury reservoir, *d*, lowered, the titrating point, *h*, and the buret to the zero point are filled with the reagent. The reagent is obviously discharged from the buret by raising the mercury level in *d*, adjusting stopcock *e* to join *f* and *h*, and using the stopcock on *h* to control the titration.

ACCURACY. The buret described above was constructed of glass tubing of slightly larger bore than that described by Conway. A delivery of 0.1 cc. represented 128 mm. on the graduated tube of his buret, while the same distance on the author's scale represents a volume of 0.145 cc. The error of delivery of the author's buret is, presumably, of similar magnitude to that given by Conway, but it may actually have been considerably lessened by using mercury to expel the fluid. The author has investigated the accuracy of the buret only for the particular purpose for which he wished to use it—namely, for titrating ferric thiocyanate.

A series of ten titrations of a standardized ferric chloride solution was made, employing a titrating vessel of the type already described (5) and carrying out the titration at 50° ($\pm 2^\circ$) with a slow stream of carbon dioxide bubbling through the solution. The volume of the solution was 20 cc. and comprised 10 cc. of the ferric chloride solution containing 0.05 mg. of Fe^{+++} , 5 cc. of 5 *N* hydrochloric acid, 4 cc. of water, and 1 cc. of 40 per cent potassium thiocyanate solution. The thiocyanate solution should not be added until just before commencing the titration. The height of the titration vessel was adjusted so that the tip of the buret was just below the surface of the liquid. The maximum variation in these titrations was equivalent to two buret divisions (0.0057 cc.) and represents an error of 2.2 per cent.

A further series of ten titrations was carried out with vary-

ing amounts of the ferric chloride solution from 1 to 10 cc. and under the conditions just described. The results showed that the same degree of accuracy can be maintained with a dilution of 15 γ of Fe^{+++} in a total volume of 20 cc. In the author's experience greater accuracy is not obtainable by using a more dilute titanous chloride solution or a smaller buret, since the sensitivity of the eye to the thiocyanate end point becomes the limiting factor.

Cobalt Nitrate Solution as a Color Standard

In the study of iron metabolism there is occasional need for an analytical procedure which can be relied upon to estimate amounts of iron of the order of 0.5 γ . Obviously volumetric methods are not applicable. Of the many colorimetric methods devised for this purpose, that recommended by Hill (3) has much to commend it. The many advantages of α, α' -bipyridine as a reagent for the microestimation of iron have been detailed by Hill.

The method has been in use in this laboratory for several years. While the author has confirmed, in every detail, the claims made for the reagent, he has not been entirely satisfied with the method of estimating the intensity of the pink color. Hill's procedure is analogous to that used for the colorimetric determination of pH and consists in preparing a series of standard tubes of varying dilutions of ferrous bi-

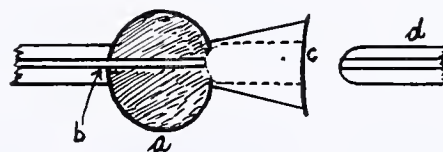


FIGURE 2. CONTINUOUS CAPILLARY JOINT

pyridine which are sealed after passing a small amount of sulfur dioxide through the solution. In the author's experience these color standards are liable to fade, particularly at high dilutions. Their preparation is also a laborious procedure which is not likely to commend itself to those desirous of making a very limited number of iron determinations in the shortest possible time.

When compared in a colorimeter, the color of a cobaltous nitrate solution matches excellently the color of ferrous bi-

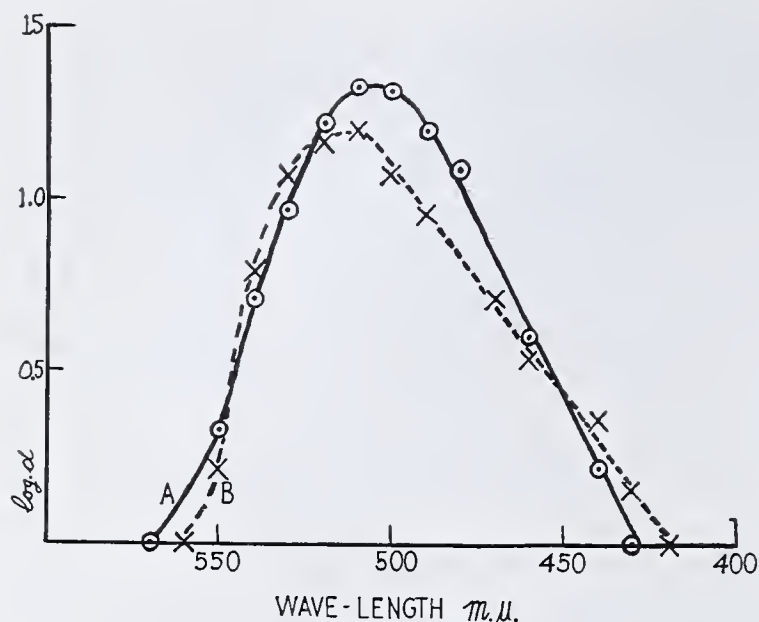


FIGURE 3. ABSORPTION CURVES

A, 2.5 per cent solution of cobalt nitrate
B, ferrous bipyridine solution containing 4.77γ of iron per cc.

The two solutions were of the same color intensity. The data were obtained with a Bellingham and Stanley direct-reading spectrometer, using 5-cm. tubes and making the density readings with an Ilford wedge.

pyridine. Both solutions show selective absorption in essentially the same region of the visible spectrum (Figure 3). Within a range of iron concentrations from 0.25 to 3.0γ per cc. the intensity of the pink color of ferrous bipyridine is directly proportional to the amount of iron present (Figure 4) and can be estimated with an accuracy of at least 10 per cent by reading against a cobalt nitrate solution containing 2.5 mg. of Co^{++} per cc. Observed through a thickness of 25 mm., a solution of cobalt nitrate containing 2.5 mg. of Co^{++} per cc. has a color intensity equivalent to that of a ferrous bipyridine solution containing 1.62γ of Fe per cc.

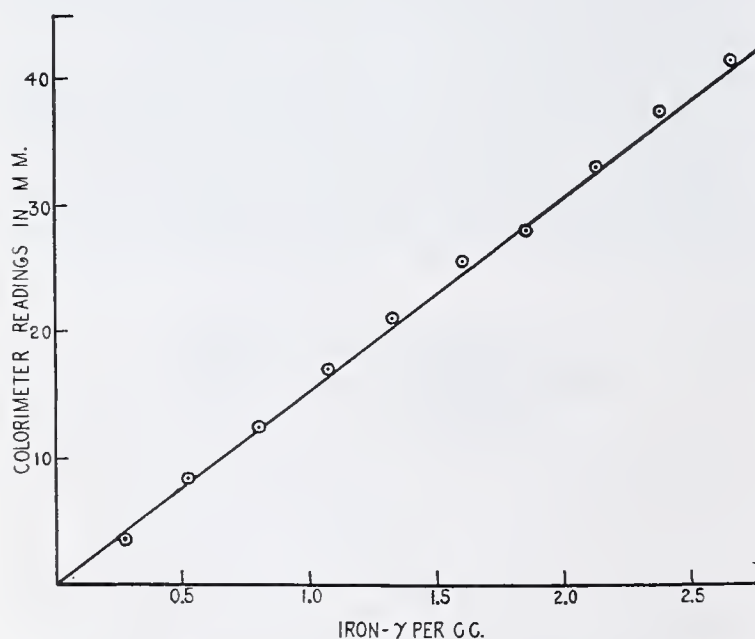


FIGURE 4. PROPORTIONALITY BETWEEN AMOUNT OF IRON PRESENT AND INTENSITY OF COLOR DEVELOPED WITH BIPYRIDINE

Values plotted represent the colorimeter readings in mm. of a cobalt nitrate solution containing 2.5 mg. of Co^{++} per cc. when the test solutions were set at 25 mm. The diagonal line represents the theoretical proportionality between iron present and color produced.

Composition of test solutions: 0.5 to 6.0 cc. of standard FeCl_3 solution containing 5.3γ of Fe per cc.; 0.25 cc. of approximately 0.004 N TiCl_3 solution; 1.0 cc. of 0.004 M α, α' -bipyridine. Diluted in each case to 10 cc. with acetate buffer, pH 4.7.

Modified Procedure

SOLUTIONS REQUIRED. Cobalt nitrate solution: 1.235 grams of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 cc. of distilled water (1 cc. = 2.5 mg. of Co^{++}). 0.004 M α, α' -bipyridine solution: 63.2 mg. of α, α' -bipyridine and 1 cc. of approximately N hydrochloric acid (prepared from redistilled hydrochloric acid) in 100 cc.

Acetate buffer, pH 4.7: equal parts of 0.2 N acetic acid (prepared from redistilled glacial acetic acid) and 0.2 N sodium hydroxide (prepared from sodium and found to contain no iron).

Approximately 0.004 N titanous chloride solution (the product of the LaMotte Chemical Co. is free from iron) or solid sodium hyposulfite freed from iron according to Hill.

PROCEDURE. An aliquot of the solution to be analyzed, preferably not exceeding 5 cc., is transferred to a 10-cc. glass-stoppered measuring cylinder and to it are added 1 cc. of bipyridine solution and 0.25 cc. of titanous chloride solution or a knife-point of solid sodium hyposulfite. It is diluted to the 10-cc. mark with acetate buffer, mixed and compared in a colorimeter with the test solution set at 25 mm., and the cobalt nitrate solution adjusted to match.

The iron content of the solution in γ per cc. is calculated from

$$\frac{\text{Reading of standard}}{25} \times 1.62$$

The colorimetry is most satisfactory within the range of 0.25 to 3.0γ of iron per cc. If it is found that the color given by the test solution exceeds this limit, the solution should be diluted with acetate buffer and the measurement repeated.

Ferrous bipyridine develops its maximum color in a few minutes only in solutions more alkaline than pH 3.5. If the solution under examination is known to be pH 3.5 or above, the use of the acetate buffer is, of course, unnecessary. Specially pure cobalt nitrate or a particularly high degree of accuracy in preparing the standard solution is unnecessary, as cobalt nitrate solutions do not conform to Beer's law in that a relatively large increase in concentration is necessary to effect much change in the color of the solution.

These modifications greatly simplify a method which, as pointed out by Hill, has many important advantages over other methods proposed for the estimation of iron. The preparation and standardization of an iron solution are now unnecessary. Special purification of the reducing agent may be avoided by substituting titanous chloride for sodium hyposulfite. Furthermore, in the author's experience (5), the colorimetry with ferrous bipyridine with the amounts of iron under consideration is a decided improvement over that with ferric thiocyanate.

Unfortunately, the reagent α, α' -bipyridine is not procurable on the market, but it may be readily prepared from α -picoline according to Blau (1). J. M. Tracy in this laboratory has found that better yields are obtained by precipitating the copper picolinate with a saturated solution of copper sulfate instead of a 1 per cent solution and that more rapid steam-distillation, resulting in better crystallization of the product, is obtained by saturating the crude bipyridine solution with sodium chloride.

Acknowledgment

The author is indebted to George Hunter for many helpful suggestions.

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Direct Titration of Sulfates

Further Studies with Tetrahydroxyquinone as an Internal Indicator

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SCHROEDER (1) recently suggested a direct titration method for sulfates with the use of tetrahydroxyquinone as an internal indicator. A direct titration method of this type offers considerable advantage over other rapid methods where outside indicators, back-titrations, or filtrations are required. The method as described by Schroeder allows the direct titration of sulfate in a sample with a standard barium chloride solution, the end point being indicated by the appearance of the red barium salt of tetrahydroxyquinone. An extensive bibliography on sulfate determinations was given in Schroeder's paper and further reference is not required at this time.

Schroeder suggested the dispersion of the tetrahydroxyquinone with a large amount of potassium chloride to give a dilution that could be readily handled by using a few tenths of a gram of the dry mixture for each determination, this dry dispersion being necessary because the solutions of tetrahydroxyquinone are not sufficiently stable to be added to the sample in this form. This method of adding the tetrahydroxyquinone to the sample was followed in the present investigation. (The prepared tetrahydroxyquinone-potassium chloride mixture has been named by this laboratory THQ and will be referred to as such throughout this paper.)

The method suggested by Schroeder limited the range of sulfate in a 25-cc. sample between 80 and 800 p. p. m. and further suggested the use of equal quantities of ethyl alcohol or alcohol denatured by formula No. 30 or 3-A to reduce the solubility of the barium sulfate and hasten the precipitation, titrating with 0.025 *N* barium chloride in a solution neutralized to the acid side of the phenolphthalein end point. Phosphate was found to be an interfering ion.

It was the aim of this investigation to extend the sulfate range, which was found possible, and to find a diluent that could be used in place of ethyl or denatured alcohol, because of the difficulty of obtaining either the ethyl or the denatured alcohol in many plants, owing to certain government restrictions. Isopropyl alcohol was found to answer this purpose. Elimination of the phosphate ion is desirable and it was found that this ion could be eliminated up to 60 p. p. m. by changing the pH value of the titrating solution to about 4.0.

Experimental

The indicator used throughout this study was manufactured in the Betz laboratory and considerable quantities of his material have been supplied to the field.

Detailed directions are given below for a determination of sulfate by direct titration using THQ as the indicator.

MATERIALS AND REAGENTS. Standard barium chloride solution, the strength varying from 1 cc. = 1 mg. of SO_4 to 1 cc. =

The direct titration method for determination of sulfates with the use of tetrahydroxyquinone as an internal indicator is described. Sulfates can be determined by this method up to 30,000 p. p. m. Phosphates up to 60 p. p. m. can be eliminated by pH control. Isopropyl alcohol is found to be as satisfactory as ethyl alcohol for reducing solubility of barium sulfate and hastening the precipitation. The use of sodium chloride to sharpen the end point in concentrations above 2000 p. p. m. of sulfate is described. Results obtained by this method check gravimetric analyses within an average of 3 per cent. Comparison of results with the Betz-Hellige method is given.

50 mg. of SO_4 , standardized gravimetrically. An indicator composed of disodium tetrahydroxyquinone ground with dried potassium chloride in a 1 to 300 ratio, and passing a 100-mesh screen. Ethyl alcohol or alcohol denatured by formula No. 30 or No. 3-A, or isopropyl alcohol. Phenolphthalein indicator and bromocresol green indicator (if phosphates are present). Sodium chloride crystals, c. p.

PROCEDURE A. Carefully neutralize a 25-cc. sample containing up to approximately 2000 p. p. m. of SO_4 with approximately 0.02 *N* hydrochloric acid until just acid to phenolphthalein. The temperature of the sample should be below 35° C. and it is advisable to work between 20° and 25° C. Add either 25 cc. of ethyl alcohol or alcohol denatured by formula No. 30 or No. 3-A or isopropyl alcohol. Introduce the THQ, the amount to be determined from Table I. It is best to use a small

cup to measure the mixture. Swirl the flask to dissolve the THQ; the solution will be colored a deep yellow. Titrate with standard barium chloride solution, the strength to be employed depending on the approximate sulfate content of the sample, in accordance with Table I. Add the standard barium chloride at a steady dropping rate with a constant swirling of the flask until the yellow color changes to a rose. The rose color should appear throughout the body of the solution and not as spots of color. This point is taken as the end point.

TABLE I. THQ REQUIRED FOR VARIOUS SULFATE CONCENTRATIONS

Sulfate Concentrations P. p. m.	Quantity of THQ Indicator Gram	Dippers of THQ Indicator	Strength ^a of BaCl_2 Solution	Sodium Chloride Crystals Required Grams
Up to 100 ^b	0.1	0.5	1	...
100 to 1000 ^b	0.2	1	1	...
1000 to 2000	0.2	1	4	...
2000 to 4000	0.4	2	10	2
4000 to 10000	0.4	2	10	4
10000 to 20000	0.6	3	50	8
20000 to 30000	0.8	4	50	8

^a 1 cc. = mg. of SO_4 .

^b Subtract 0.1 cc. as a blank in titration.

PROCEDURE B (sulfate range from 2000 to 30,000 p. p. m.). Add solid sodium chloride to the sample in an approximate amount as given in Table I. The procedure is the same as in A for neutralization and titration.

PROCEDURE C (with phosphate ion present up to 60 p. p. m.). Carefully neutralize a 25-cc. filtered sample with approximately 0.02 *N* hydrochloric acid until just acid (yellow range) to bromocresol green (approximate pH 4). Follow procedure as in A or B; no correction will be required for the phosphate ion present.

The titration procedure employed was identical with that proposed by Schroeder. The end point is taken as the appearance of rose throughout the body of the solution, and is somewhat similar to a methyl orange end point in alkalimetry. To facilitate observation of the end point, a strong side illumination with a lamp was employed. It was found that because of the quantities of barium sulfate resulting, in higher concentrations of sulfates, either an adsorption of the indicator occurred or the end point was masked. To overcome this difficulty, additional quantities of the indicator

TABLE II. TITRATION OF SODIUM SULFATE

(All titrations were carried out at pH 8.3. 25 cc. of ethyl alcohol, denatured with No. 3-A or 30, were used.)

SO ₄ Present P. p. m.	SO ₄ Found P. p. m.	Error %	THQ Gram	BaCl ₂ Used Cc.
1 cc. = 1.04 mg. of SO ₄ ^a				
20	19.9	-0.5	0.1	0.48
40	37.5	-6.3	0.1	0.90
77.6	74.9	-3.5	0.1	1.80
101	98	-3.0	0.2	2.35
202	204	+1.0	0.2	4.90
404	399	-1.1	0.2	9.60
485 ^b	466	-4.0	0.2	11.20
504	516	+2.4	0.2	12.30
1 cc. = 4.07 mg. of SO ₄				
620	602	-2.9	0.2	3.65
907	904	-0.3	0.2	5.55
1550 ^b	1547	-0.2	0.2	9.50
1605	1612	+0.4	0.2	9.90
2132	2096	-1.7	0.2	12.85
3019	3030	+0.3	0.4	18.00
1 cc. = 10.49 mg. of SO ₄				
2403	2308	-3.9	0.4	5.50
3876	4016	+3.7	0.4	9.57
5426	5509	+1.7	0.4	13.13
5426 ^b	5287	-2.5	0.4	12.60
7558	7343	-2.8	0.4	17.50
9690 ^b	9441	-2.5	0.4	22.50
1 cc. = 52.45 mg. of SO ₄				
10856	11015	+1.4	0.6	5.25
15508	15106	-2.6	0.6	7.20
15508 ^b	15735	+1.4	0.6	7.50
21711 ^b	20980	-3.4	0.8	9.95
34117	32729	-4.0	1.0	15.60

^a 0.1 cc. blank was subtracted from values obtained when 1 cc. of BaCl₂ = 1.04 mg. of SO₄.

^b 25 cc. of isopropyl alcohol.

were added to allow the proper observation of the end point. The character of the color of the end point changed somewhat, owing to the presence of the precipitated barium sulfate, becoming more intense in higher concentrations. The results obtained are presented in Table II.

Isopropyl alcohol was used on some samples as indicated with equally successful results. Standard dippers were employed to measure the THQ indicator, each dipper holding 0.2 gram of the indicator. The results presented in Table II show that the method is applicable for the determination of sulfates up to approximately 30,000 p. p. m. of sulfate or approximately a 3 per cent solution of sulfate. All titrations in the tables are averages of two or more values, none of the volumes of barium chloride used deviating from each other by more than 3 per cent. An arithmetical average of forty-two determinations gave a 2.4 per cent error; twelve results of the forty-two were high, showing that in general results had a tendency to be slightly low. It has been found advantageous to use varying amounts of the THQ depending on the sulfate range in which the determination is being made (Table I).

Several other diluents besides isopropyl alcohol were tried and found unsatisfactory, including diacetone, furfural, formaldehyde, normal butyl and isobutyl alcohol, and acetone. Acetone at first gave some promise but the end point was not as clear as with either alcohol or isopropyl alcohol and results were not as accurate and further work on this diluent was abandoned. Schroeder investigated the effects of ions and mixtures of ions in synthetic solutions and stated that at least 320 p. p. m. of CO₃⁻⁻, 200 p. p. m. of Al⁺⁺⁺, 1020 of SiO₃⁻⁻, 400 of Mg⁺⁺, 200 of Ca⁺⁺, and 200 of OH⁻ could be tolerated without interference with the method. He also stated that PO₄⁻⁻⁻ required excess barium chloride, owing to the insolubility of some barium salt of PO₄⁻⁻⁻, and could be corrected by subtracting a blank from the total titration, the value of the blank depending on the quantity of PO₄⁻⁻⁻ present.

Serious drawbacks to the correction method for phosphate advanced by Schroeder are: (1) the phosphate content must be known and (2) corrections must be made for each strength of barium chloride titrating solution. Schroeder was working with only one strength of barium chloride but this investigation, covering a larger range of sulfate, required several strengths and would therefore require several correction factors for phosphate.

The complete removal of the PO₄⁻⁻⁻ by the aid of metals whose phosphates were insoluble and whose sulfates were soluble was attempted. It was found that other complications, such as the insolubility of oxides and hydrates of the metal and destruction or coloring of the THQ by these other metals and the precise control of the quantity or concentration of the metals required, were insurmountable obstacles for practical application.

Knowing that different barium salts of *o*-phosphoric acid form at different pH values, it was decided to attempt to form a more soluble salt at a lower pH. The following procedure was employed, using bromocresol green as indicator: The sample was neutralized just to the yellow range of the indicator, 25 cc. of alcohol were added and then the THQ. The THQ was stable in such a solution for at least 20 minutes, which is considerably in excess of time to complete the titration in a satisfactory fashion. Solutions with various sulfate and phosphate contents were titrated and it was found that by this procedure up to 60 p. p. m. of PO₄⁻⁻⁻ could be tolerated without interference, and above this value excess barium chloride solution was required to obtain the end point. Table III shows the results obtained by this procedure for elimination of interference by phosphates.

In using this lower pH value, care must be exercised to prevent excess acid being added to the solution, as such will destroy the THQ. Naturally, in titrating, the pH value of the solutions will gradually rise as the standard barium chloride employed has an approximate pH value of 7.0. The color of the titrating medium will therefore change slightly on account of the bromocresol green present, taking on a greenish tinge with a rise in pH value. This can be discharged by a drop or two of the 0.02 *N* hydrochloric acid. The intensity of the green color was held at a minimum by use of 0.1 cc. of 0.04 per cent bromocresol green, which was found sufficient to observe the neutralization. Where work is conducted continuously at this lower pH value, it might prove advantageous to buffer the barium chloride standard solution at a lower pH.

TABLE III. PHOSPHATE ELIMINATION BY pH CONTROL

(pH 4. 1 cc. of BaCl₂ = 1.04 mg. of SO₄. 0.1 cc. blank subtracted from values when 1 cc. of BaCl₂ = 1.04 mg. of SO₄.)

SO ₄ Present P. p. m.	SO ₄ Found P. p. m.	Error %	PO ₄ Present P. p. m.	BaCl ₂ Used Cc.
98.8	99.8	+1.0	17.6	2.40
98.8	99.8	+1.0	35.2	2.40
98.8	100.8	+2.0	62	2.42
97	108	+11.3	79	2.60
97	114	+17.5	92	2.75
415 ^a	415	0.0	62	3.90

^a 1 cc. of BaCl₂ = 4.07 mg. of SO₄.

Schroeder found that in each titration 0.1 cc. blank should be subtracted. This was necessary only when using the standard barium chloride where 1 cc. of barium chloride equals 1 mg. of SO₄. The only ions giving interference were Fe⁺⁺⁺, Fe⁺⁺, Al⁺⁺⁺, and PO₄⁻⁻⁻ in excess of 60 p. p. m. Iron in both the ferrous and ferric state must be maintained lower than approximately 5 p. p. m. This is not considered a serious drawback to the method, as in boiler waters soluble iron will seldom be found to this extent with higher pH values, most iron being present in the insoluble form. Where iron is present in a sample, it should be removed prior to titra-

TABLE IV. EFFECT OF SINGLE IONS AND OTHER MATERIALS (pH 4. 25 cc. of isopropyl alcohol used. 0.1 cc. of blank subtracted from values when 1 cc. of BaCl₂ = 1.04 mg. of SO₄. Cl as listed was in excess of Cl as derived from KCl in the THQ prepared indicator.)

SO ₄ Present P. p. m.	SO ₄ Found P. p. m.	Error %	BaCl ₂ Used Cc.	Ion Present P. p. m.
1 cc. of BaCl ₂ = 1.04 mg. of SO ₄ ; 0.2 gram of THQ				
97	98	+1.0	2.40	PO ₄ 62
97	100	+3.0	2.40	Fe ⁺⁺⁺ 6.4
98.8	100	+1.2	2.40	Fe ⁺⁺ 4
98.8	100	+1.2	2.40	SiO ₃ 1500
98.8	98.8	0.0	2.35	Tannin 80
98.8	100	+1.2	2.40	Mg 120
98.8	98	-0.8	2.38	Ca 344
98.8	96	-2.8	2.30	Ca 688
98.8	98	-0.8	2.35	Cl 3920
98.8	133	+34.8	3.20	Cl 15680
1 cc. of BaCl ₂ = 4.07 mg. of SO ₄ ; 0.2 gram of THQ				
1646	1620	-1.6	9.95	PO ₄ 62
1646	1652	+0.4	10.15	Fe ⁺⁺⁺ 8.0
1646	1645	0.0	10.10	Fe ⁺⁺ 5.8
1646	1610	-2.2	9.90	SiO ₃ 1500
1646 ^a	1628	-1.1	10.00	Tannin 80
1646	1669	+1.4	10.25	Mg 1440
1646	1628	-1.1	10.00	Ca 344
1646	1661	+0.9	10.20	Cl 7840
1646	1677	+2.0	10.30	Cl 47040
1 cc. of BaCl ₂ = 52.45 mg. of SO ₄ ; 0.6 gram of THQ				
13160 ^{b,c}	13108	-0.4	6.20	PO ₄ 62
13160	12798	-2.7	6.10	Fe ⁺⁺⁺ 8.0
13160	12798	-2.7	6.10	Fe ⁺⁺ 5.8
13160	13467	+2.3	6.40	SiO ₃ 1500
13160 ^{a,c}	13217	+0.4	6.30	Tannin 80
13160 ^a	12798	-2.7	6.10	Tannin 80
13160 ^{b,c}	12798	-2.7	6.10	Al 6.0
13160	13647	+3.5	6.50	Mg 1440
13160 ^b	13008	-1.2	6.20	Ca 344
13160	13008	-1.2	6.20	Ca 344
14160	12798	-2.7	6.10	Cl 23520

^a 0.5 cc. of bromocresol green used in neutralization because of brown color from tannin.
^b 6 grams of NaCl used in titration.
^c 25 cc. of ethyl alcohol denatured by No. 3-A or 30.

tions, as otherwise the THQ is colored green and destroyed. The results with Al⁺⁺⁺ show that even 6 p. p. m. cannot be tolerated in lower sulfate concentrations. Here again, little difficulty is expected, as soluble Al⁺⁺⁺ is seldom found in appreciable concentrations in boiler waters. In higher sulfate concentrations (about 13,000 p. p. m.) 6 p. p. m. of Al⁺⁺⁺ can be tolerated. It is believed that the sulfate content is only indirectly responsible for this and probably the higher concentrations of the tetrahydroxyquinone required overcome the interference with the Al⁺⁺⁺. Tolerances of the various other ions studied were in general high and in water work at least will exert no influence on the method. SiO₃⁻⁻⁻ can be tolerated up to 1500 p. p. m., tannin up to 80, Mg⁺⁺ at least 1440, Ca⁺⁺ to at least 344, and higher depending on the sulfate content (one of these two variables determines the tolerance of the other, due to the solubility of calcium sulfate in the system), and Cl⁻ up to 15,000 and higher depending on the sulfate content. Above 2000 p. p. m. of sulfates, sodium chloride can be used advantageously to sharpen the end point (Table V).

The effect of temperature was studied and it was found that the temperature of the sample should be held below 35° C. Higher temperatures destroy the indicator.

It was realized that detection of the end point in this titration might prove difficult for inexperienced or nontechnical operators, and several agents were investigated that might tend to give a more readily discernible end point under all conditions. The use of xylene cyanole, a green dye, was investigated and found to be of no aid in this work. This dye was selected because of its possible application in clarifying the methyl orange end point in alkalimetry work.

In the higher sulfate concentrations, the end point might be termed as somewhat "sliding"—that is, the solution starts to change color before all the sulfate is stoichiometrically precipitated, probably because the increased amount of THQ required promotes the reaction between the indicator

and the barium ion. To eliminate this difficulty, the use of sodium chloride was found advantageous. It has been determined that any agent furnishing sodium ion and not interfering otherwise with the titration could be employed. A small amount of the solid sodium chloride added to the solution where the sulfate concentration was above 2000 p. p. m. not only caused a very rapid change of color at the end point, but considerably increased the accuracy of the determination in this range. However, with sulfate concentrations materially below 2000 p. p. m., high results were obtained, due to a delayed end point. The results in higher ranges with the use of this sodium chloride are presented in Table V.

TABLE V. EFFECT OF NaCl FOR SHARPENING THE END POINT

SO ₄ Present P. p. m.	SO ₄ Found P. p. m.	Error %	BaCl ₂ Used Cc.	NaCl Used Grams
1 cc. of BaCl ₂ = 1.04 mg. of SO ₄ ; 0.2 gram of THQ				
pH 8.3				
97	108	+11.0	2.60	0.5
97	106	+9.0	2.55	0.2
291	408	+4.0	9.80	1.0
1 cc. of BaCl ₂ = 10.49 mg. of SO ₄ ; 0.4 gram of THQ				
3292	3273	-0.6	7.80	2.0
6584	6630	+0.7	15.80	2.0
1 cc. of BaCl ₂ = 52.45 mg. of SO ₄ ; 0.6 gram of THQ				
13160	13113	-0.4	6.25	4.0
19740	19511	-1.2	9.30	4.0
26320	25805	-2.0	12.30	15.0
26320	26015	-1.1	12.40	5.0
32900	32519	-1.2	15.50	5.0
32900	32834	-0.2	15.65	10.0
pH 4				
13160	13113	-0.4	6.25	10.0

0.1 cc. blank subtracted when 1 cc. of BaCl₂ = 1.04 mg. of SO₄. 25 cc. of ethyl alcohol denatured with No. 3-A or 30.

TABLE VI. RESULTS OBTAINED ON ACTUAL BOILER- AND FEED-WATER SAMPLES

Sample	Sulfate Found			Percentage Error Based on Gravimetric	
	Gravimetric	THQ	Betz-Hellige	THQ	Betz-Hellige
1	9.1	9.4	8.7	+3.3	-4.4
2	206	204	205	-1.0	+0.5
3	22	27	21	+22.7	-4.4
4	722	712	700	-1.4	-3.0
5	1461	1458	1400	-0.2	-4.0
6	9833	9492	9700	-3.4	-1.3
7	2315	2277	2250	-1.7	-2.8
8	66	61	67	-7.6	+1.5
9	2193	2214	2150	+1.0	-2.0
10	23602	24337	22500	+3.1	-4.7
11	484	494	455	+2.1	-6.0

Only a few tests were made adding sodium chloride with sulfate concentrations below 2000 p. p. m., but these were sufficient to indicate that a delayed end point producing high results was obtained. The effect of the sodium chloride when a titration is carried at pH 4 and in the presence of various ions was found to give the same results as at pH 8.3.

The final test of the method was obtained by comparing results by titrations of a number of boiler-water samples to results obtained by gravimetric analysis and precipitation as barium sulfate. A comparison of results was also made by the Betz-Hellige method recently proposed (2), this being particularly applicable to accurate sulfate determinations in lower concentrations. As the sulfate content of boiler water samples will not usually run above 2000 to 3000 p. p. m., and it was desired to test above this range, some samples containing a fairly high sulfate content were taken and concentrated by evaporation.

Fairly good agreement was obtained throughout the range, the percentage error being greater in the lower concentrations. Below 100 p. p. m., greater accuracy will be obtained by the Betz-Hellige method, while in the higher concentrations, the

tetrahydroxyquinone gives the better result. Results can be expected to check with gravimetric with an average of about 3 per cent error.

TABLE VII. ANALYSIS OF SOLUTIONS USED

Sample	Total Hardness	Cl	HCO ₃	CO ₃	OH	Dis-solved Solids	Fe	SiO ₂	PO ₄	pH
	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	P. p. m.	
1	24	4	14	700	57	6.7
2	40	72	..	56	40	57	10.9
3	58	12	60	6.9
4	12	224	..	216	72	2208	0.5	30	11	11.1
5	2	496	..	448	156	4432	11.5
6	0	1408	..	2552	320	19330	1.5	4	0	11.9
7	2	116	..	116	762	5700	0.5	6	0	11.9
8	88	12	29	6.9
9	0	254	..	152	540	5932	0.5	19	25	11.9
10	Analysis about same as No. 9.					SO ₄ increased by Na ₂ SO ₄				
11	13	190	..	264	62	57	11.1

During the past 3 months over 5000 water samples have been analyzed in the Betz laboratories employing the tetrahydroxyquinone method for the sulfate determination. Over ten operators are employed in this work and no difficulty has been experienced with this method.

Conclusions

The tetrahydroxyquinone method for sulfate determination has been shown to be accurate up to approximately 30,000 p. p. m. or a 3 per cent solution of SO₄. Isopropyl alcohol can be used with equally accurate results in place of ethyl alcohol for lowering the solubility of the barium sulfate and hastening the precipitation. The phosphate ion, up to 60

p. p. m., can be tolerated by adjusting the pH value of the sample before titration to approximately 4.0 with the aid of bromocresol green as an indicator. With the exception of iron and aluminum, other ions normally present in boiler feed waters give no difficulty. It was found that solid sodium chloride could be used to advantage to sharpen end points with sulfate concentrations above 2000 p. p. m. A comparison of gravimetric, tetrahydroxyquinone, and Betz-Hellige methods on boiler-water and boiler-feed samples shows that acceptable results in all concentrations were obtained. It is believed that this method of sulfate determination will have possible application in determination of sulfates in fuel, cement, rubber, and numerous other fields.

Acknowledgment

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Determination of Sulfate

An Attempt to Determine Sulfate by Titration with Lead Nitrate, Using Eosin as Indicator

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THIS is a report of an attempt to titrate sodium or potassium sulfate directly with standard lead nitrate solution, using eosin as indicator. The work arose from a problem of analysis in the phase-rule study of certain systems involving sulfates, in which it was desired to find a rapid method for the direct determination of the sulfate.

A titration with lead nitrate in the presence of some potassium iodide as internal indicator, using the appearance of the yellow lead iodide as the end point, was attempted first; after considerable work on this method, it was given up as impracticable. The writer then learned that the method had been suggested as far back as 1853 by Levol (8), and subsequently by several other chemists since that date (5, 10, 12), and that the same conclusion had been reached as to its inadequacy by other investigators who examined the method (7, 9, 11). (Levol was also the first to announce, in 1853, this type of titration even for chloride, using the appearance of yellow silver phosphate as the end point, instead of silver chromate, in an otherwise typical "Mohr" titration.) The use of potassium iodide paper as an external indicator for this titration is known as Pappenheim's method (11), and although it was criticized as impracticable by Mohr (11), Vinogradov (18) as recently as 1935 found it the best of the volumetric methods for the determination of sulfate by means of lead salts. The only other applications of lead salts in the volumetric determination seem to be in certain electrometric methods (14, 20), and in indirect methods, in which the sul-

fate is precipitated with an excess of lead nitrate (13) or lead acetate (4), and the excess of lead salt is titrated by chromate or molybdate, respectively. Roy (15), suggesting the titration of lead by means of sulfate with fluorescein as external indicator, mentions the possibility of using such a titration for the indirect estimation of sulfate. Apparently, however, no method has yet been suggested for the direct titration of sulfate with lead salts by means of an adsorption indicator. The reader is referred elsewhere for reviews of the volumetric methods for sulfate, most of which involve the use of barium chloride as standard solution (1, 16).

Suggested Method

The present method makes use of eosin as an internal indicator for the direct titration of sodium or potassium sulfate with standard lead nitrate solution. The end point is indicated by the appearance of the red lead salt of eosin, C₂₀H₆Br₄O₅Pb (2), bringing about a change from the yellowish flesh color of the mixture of precipitate and solution to a light but distinct pink-red. The following solutions were used:

The sodium and potassium sulfate solutions were prepared from c. p. anhydrous salts, and standardized by evaporation to dryness at 250° C. and direct weighing of the residue. Strengths used were from 0.1 M to 0.32 M.

The lead nitrate solutions, also prepared from c. p. reagent material, were standardized by treating a measured volume with a known weight of pure potassium iodate, filtering off the pre-

precipitate of lead iodate and determining the excess potassium iodate by adding excess of potassium iodide and sulfuric acid to the filtrate and titrating the liberated iodine with sodium thiosulfate solution previously standardized against the same pure potassium iodate. The values so obtained were checked by repeating the procedure, using pure potassium chromate instead of potassium iodate, and also by the gravimetric method of precipitating and weighing lead chromate. Another method used for standardizing the lead nitrate solution was evaporation to constant weight at 85° to 90° C.

The indicator solution was a 0.5 per cent solution of eosin Y, $C_{20}H_6Br_4O_5Na_2$, in water.

The results given in A, Table I, and in Table II are from a series of titrations of 0.1 M sodium sulfate with 0.1 M lead nitrate, using 12 drops of indicator, the procedure being as follows:

The sodium sulfate solution (from 6 to 20 cc.) is measured by buret into a 250-cc. Erlenmeyer flask, enough water being added, if necessary, to bring the total volume at the end point of the titration to 30 cc. After the addition of 12 drops of indicator, the lead nitrate solution is run into the flask drop by drop, with vigorous shaking. When a certain amount of lead sulfate has been precipitated, as by the addition of 2 to 3 cc. of the lead solution, the whole mixture is something between yellow and flesh color. Each drop of the lead solution causes a red coloration which disappears into the comparative yellow color of the mixture on shaking and mixing. The end point is the appearance and persistence of a distinct pink throughout the mixture. It is most important that the titration be finished very slowly and with vigorous shaking to insure the re-solution of the red lead-eosin salt formed by each drop added as the end point is approached.

The best results are obtained with the use of a reference color, with approximately the same amount of lead sulfate in it as will be present in the sample being titrated, prepared by mixing equivalent volumes of the lead nitrate and sodium

sulfate solutions, with the same amount of indicator and in the same total volume. With some practice, however, the end point is distinct enough even without a reference color. The results summarized in Table II were obtained some with and some without such a reference; out of 72 titrations, 7 gave bad results and were omitted in making up this table.

Effect of Variations

Owing, of course, to the relatively high solubility of lead sulfate and to the properties of both the eosin solution and the lead-eosin compound formed, the end point of such a titration will be markedly affected by changes in conditions, such as total volume, presence of foreign salts, etc. Some study was made of the effect of the variations of these factors with the following results:

TOTAL AMOUNT OF SULFATE THAT CAN BE TITRATED. The best range is from 0.1 to 0.15 gram of SO_4^{--} ; the maximum amount is about 0.2 gram, the equivalent of about 18 to 20 cc. of 0.1 M lead nitrate solution. Beyond this the titration is too doubtful. The quantity of precipitated lead sulfate becomes so great as to obscure the color change required for the end point.

TOTAL VOLUME AT END POINT. In the titrations reported in Table II, the total volume at the end point was 30 cc. in each case, except where the sum of the two solutions themselves amounted to more. If the final volume is much above 30 cc., the colors are diluted too much, so that it is again difficult to detect the end-point change. However, some variation is possible. Thus, with 40 cc. as the final volume, 10 titrations (with no omissions), using in each case about 15 cc. of the 0.1 M lead nitrate solution and with no foreign salts present, gave a relative error of 0.4 per cent as an absolute average and +0.11 per cent as the algebraic average, with extremes of -0.5 and +0.7 per cent. Some of these results are listed in Table I, B.

STRENGTH OF TITRATING SOLUTION. In the present work various concentrations of the lead nitrate were tried as titrating solutions, from 0.1 M to 0.5 M. The best results as a whole (most widely applicable and reproducible) were obtained with 0.1 M lead nitrate, the results for which are reported in Table II. If a stronger solution of lead nitrate is used in titrating, although the end point is sharper, the relative errors remain the same, since the total amount of sulfate that can be titrated also remains the same as with the 0.1 M solution—that is, a maximum of the equivalent of 8 to 9 cc. of 0.2 M solution. With 19 runs using 0.2 M solution, with a total volume at the end point of 30 cc. again, the average absolute error was 0.47 per cent, and the algebraic average error +0.23 per cent.

INDICATOR TO BE USED. The quantity of indicator recommended, 12 drops of 0.5 per cent eosin, was also determined by experiment, and is intended for the amounts of sulfate indicated in Table II. For smaller amounts of sulfate it is better to use proportionately less indicator, and a proportionately smaller final volume at the end point.

EFFECT OF ALCOHOL. It was hoped that alcohol, through its effect on the solubility of lead sulfate, might cause the end point to be sharper, an effect found by Nikaido (12) in the attempt to use potassium iodide as indicator in the titration of sulfate with lead nitrate. In the present method, however, because of its effect on the color of eosin solution and apparently also on the solubility or stability of the lead-eosin compound, alcohol in amounts greater than 3 to 4 per cent is found to interfere, delaying the end point so much that the titration becomes impossible. With smaller amounts of alcohol, while there is no appreciable interference there is at the same time no improvement in the titration.

EFFECT OF DEXTRIN. The addition of dextrin as a protective colloid was also tried, inasmuch as the color to be ob-

TABLE I. RESULTS OF TYPICAL TITRATIONS
(Using 0.1 M lead nitrate)

	Total Volume Cc.	Foreign Salts Grams	Na ₂ SO ₄ Present Gram	Na ₂ SO ₄ Found Gram	Error Gram	Per Cent Error
A	30	None	0.0878	0.0881	+0.0003	+0.3
	30	None	0.0910	0.0909	-0.0001	-0.1
	30	None	0.1341	0.1339	-0.0002	-0.2
	30	None	0.1594	0.1588	-0.0006	-0.4
	30	None	0.1610	0.1613	+0.0003	+0.2
	30	None	0.1751	0.1745	-0.0006	-0.3
	30	None	0.1778	0.1781	+0.0003	+0.2
	30	None	0.2104	0.2098	-0.0006	-0.3
	30	None	0.2661	0.2673	+0.0012	+0.5
B	40	None	0.2185	0.2184	-0.0001	.0
	40	None	0.2186	0.2192	+0.0006	+0.3
	40	None	0.2201	0.2214	+0.0013	+0.6
	40	None	0.2185	0.2174	-0.0011	-0.5
		NaClO ₃				
C	30	0.5	0.1762	0.1768	+0.0006	+0.3
	30	1.0	0.1762	0.1767	+0.0005	+0.3
	30	1.5	0.1732	0.1723	-0.0009	-0.5
	30	2.0	0.1766	0.1769	+0.0003	+0.2
D	40	0.2	0.2185	0.2198	+0.0013	+0.6
	40	0.6	0.2202	0.2207	+0.0005	+0.2
	40	0.6	0.2214	0.2222	+0.0008	+0.4
		NaNO ₃				
E	30	0.1	0.1743	0.1744	+0.0001	+0.1
	30	0.5	0.1773	0.1777	+0.0004	+0.2
	30	1.0	0.1763	0.1767	+0.0004	+0.2
	30	0.05 NaCl	0.2215	0.2215	0.0000	0.0
	30	0.02 KI	0.2143	0.2140	-0.0003	-0.1

TABLE II. TITRATION OF 0.1 M Na₂SO₄ WITH 0.1 M Pb(NO₃)₂
(No foreign salts, total volume 30 cc.)

No. of runs	65
Na ₂ SO ₄ titrated, grams	0.08 to 0.28
Pb(NO ₃) ₂ used, cc.	6 to 20
Errors, grams of Na ₂ SO ₄ :	
Extremes	-0.0012 to +0.0015
Absolute average	0.00055
Algebraic average	-0.00004
Errors, per cent of Na ₂ SO ₄ :	
Absolute average	0.33
Algebraic average	-0.03

served is always that of the mixture of precipitate and solution, but again with no improvement; small amounts do not interfere, while larger amounts cause the end point to appear too soon.

EFFECT OF ACIDITY. The solution must be neutral. The slightest quantity of free acid or base interferes with the normal operation of the indicator. Perhaps a neutralizing buffer could be found which would make the titration possible in such cases, but this was not attempted in this work.

EFFECT OF FOREIGN SALTS (Table I, C, D, E). The effect of certain added salts was also studied, and it was found that potassium and sodium chlorate would not interfere if not more than 1 to 2 grams were present. Thus, with from 0.1 to 2.0 grams of sodium chlorate present, in 27 titrations involving 11 to 16 cc. of 0.1 *M* lead nitrate, the relative error found was 0.35 per cent as absolute average, and +0.29 per cent as the algebraic average, with extremes of -0.2 to +0.8 per cent. Up to 1 gram of sodium or potassium nitrate did not interfere: Using 0.1 to 1.1 grams of sodium nitrate in 11 runs requiring from 12 to 15 cc. of the 0.1 *M* lead nitrate solution, the algebraic relative error was +0.32 per cent with extremes of -0.2 to +0.9 per cent. A few tests also showed that 0.05 gram of sodium chloride and 0.02 gram of potassium iodide likewise did not interfere: errors: 0.0, 0.1 per cent. Finally, in experiments with the stronger titrating solution (0.2 *M*) the effect of added salts was found to be about the same as with the 0.1 *M* solution.

In these titrations with foreign salts present, the reference color used in each case was that for a mixture containing approximately the same quantity of the foreign salt.

Conclusion

In comparison with certain other similar methods recently suggested for the direct titration of sulfate, the method is similar in principle to that of Schroeder (titration with barium chloride, with tetrahydroxyquinone as internal indicator, 16) and to that of Strebing and Zombory (an indirect method using sodium rhodizonate as indicator, 17). Schroeder's method applies to quantities of 2 to 20 mg. of sulfate, while the eosin-lead nitrate titration works best for much larger quantities. (Ampt, 1, reports no success in attempts to repeat Schroeder's procedure.) Batchelder and Meloche (3) have reported experiments on the titration of sulfate with barium chloride, using methyl red as a hydrolytic adsorption indicator, with a relative error of 3 per cent in the titration. The method of Wellings (19), in which sulfate is precipitated with standard barium hydroxide in the presence of Mg^{++}

or Mn^{++} and with fluorescein as adsorption indicator, involves an average relative error, in the published results, of ± 0.45 per cent in 13 analyses. This is about the same as the error in the procedure here reported, and although Wellings' method appears to have a wider applicability, the end point, according to Iyer (6), is not sharp, and becomes "very indistinct" in the presence of potassium chloride and potassium nitrate.

Summary

From 0.10 to 0.25 gram of sodium sulfate may be determined by direct titration with 0.1 *M* lead nitrate solution in a total (final) volume of 30 to 40 cc., using 12 drops of 0.5 per cent eosin as indicator. The solution to be titrated must be neutral. The best results are obtained in the titration of about 0.15 to 0.20 gram of sodium sulfate and with the use of a reference color. The determination is then accurate to about 0.0005 gram of sodium sulfate. The presence of 1 gram of alkali nitrate or 2 grams of alkali chlorate does not interfere.

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Gravimetric Determination of Selenium in Alloy Steel

Copper Chloride-Perchloric Acid Method

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SELENIUM, like sulfur (2), may be separated from alloy steels by solution of most of the iron, chromium, nickel, etc., in copper-potassium chloride reagent. The method of attack (1) has been by (1 to 1) hydrochloric-nitric acid. Perchloric acid is added, the solution is fumed, cooled and diluted, and the silica is filtered off. The filtrate is made 30 per cent acid by volume with hydrochloric acid, sulfurous acid is added in excess, and the selenium is thus separated and filtered off on a Gooch, dried at 105° C., and weighed.

Copper Chloride Method

Transfer 5 grams of the steel (up to 0.4 per cent of selenium) to a 600-cc. beaker, and add about 500 cc. of the copper chloride. Place the beaker on a steam bath and stir frequently. With electrical stirring the sample is dissolved in less than 45 minutes. Filter the precipitate on paper and wash with hot water, then return the paper to the beaker. The paper contains all the carbon, sulfur, and selenium, but only portions of the iron, chromium, and silica. Add 10 cc. of the zinc oxide-nitric acid solution, 50 cc. of water, and 15 cc. of perchloric acid and evaporate the solution to perchloric acid fumes. Formation of chromic

acid indicates sufficient heating. Cool the beaker, add 50 to 60 cc. of water with shaking, and boil out the chlorine. Filter off the silica and wash with hydrochloric acid (1 to 1) and water. The volume of the filtrate is 100 to 125 cc. Add 100 to 125 cc. of concentrated hydrochloric acid and 100 cc. of strong sulfurous acid. Heat the beaker on a steam bath for 3 hours, then cool. Filter the selenium on a Gooch, wash with hydrochloric acid (1 to 1), then water. Dry the crucible at 100° C., then weigh, ignite, and weigh again. The loss in weight is selenium.

SOLUTIONS. Zinc oxide-nitric acid reagent: 200 grams of zinc oxide sifted into 1 liter of concentrated nitric acid. Copper chloride reagent: 500 grams of $(KCl)_2 \cdot CuCl_2 \cdot 2H_2O$, 100 cc. of hydrochloric acid, and 2000 cc. of water.

The advantages of the copper chloride solution method are: The bulk of the silica is removed in the first filtration, so that only a small amount of silica need be washed for selenium as compared to the large amounts of gelatinous silica in the acid attack method.

In the precipitation of the selenium, only about 1 gram of possible contaminants is likely to be present as compared to 5 grams in the acid attack method.

While an extra filtration is required, less attention is needed, and less time is required for fuming and for acid treatment.

TABLE I. SELENIUM DETERMINATIONS

Sample	Acid solution	Selenium Found	Copper chloride
	%	%	%
1	0.25, 0.26 ^a	0.26, 0.26	
2	0.38, 0.37 ^b	0.38	
3	0.35, 0.36 ^b	0.38	
4	0.26, 0.26, 0.26, 0.25	
5 ^c	0.32	

^a Contractor, 0.24 per cent selenium.

^b R. C. Coburn, chief chemist, Navy Laboratory, Munhall, Pa.

^c Contractor, 0.31 per cent selenium.

Table I gives data on check determinations. Small size of samples prevented more extensive checks.

Summary

Both sulfur and selenium are successfully separated from alloy steels by the copper chloride solution method. The method has several advantages over the aqua regia solution attack.

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Detection of Rhenium in the Sodium Carbonate Bead

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THE blowpipe reactions of rhenium have been investigated by Geilmann and Wrigge (2), who conclude that 0.05 per cent of the metal can be detected by heating a 10-mg. concentrate in an open tube, reducing the sublimate with sulfur dioxide, and observing the color of the deposited film. They also describe the behavior of the element in beads of molten borax, in anhydrous sodium thiosulfate, and in a mixture of sulfur and sodium carbonate, in all of which the rhenium salts form black dispersions or films of either the metal or the sulfide. The fact that manganese compounds produce a characteristic green coloration with fused sodium carbonate suggested that salts of the homologous element, rhenium, might also produce a color reaction in the sodium carbonate bead that would be serviceable in the identification of the metal.

On fusing a minute fragment of potassium perrhenate with anhydrous sodium carbonate, the bead assumes a black color which persists for about 1 minute, measured from the time of the disappearance of the initial red glow. The color of the bead then changes to yellow, the intensity of which slowly diminishes and disappears entirely at the end of about 10 minutes. Reheating the colorless bead in the flame, the same set of color transformations is observed. The formation of the black bead was also observed by Geilmann and Wrigge, who employed a mixture of sulfur and sodium carbonate as the flux.

The color changes, black-yellow-white, are given by rhenium compounds when the bead is heated either in the Bunsen flame or in the oxidizing or reducing flames produced with the blowpipe. The intensity is not influenced by the addition of oxidizing agents like potassium nitrate or chlorate, as is the case with the green manganate compound formed under the same conditions.

The yellow color of the bead is not due to sodium rhenate,

Na_2ReO_4 , as might be expected from the similar reaction in the case of manganese, for that compound possesses a green color and is unstable at high temperatures (?). Since the color of the rhenium bead is the same in both the oxidizing and reducing flames, it would seem that the formation of the yellow compound is not attended with a change in valence. I. and W. Noddack have observed that when potassium perrhenate is fused with sodium hydroxide in the presence of excess air, a yellow-colored compound is formed in which the rhenium possesses the same valence as in the original perrhenate salt, and have demonstrated that the yellow salt thus formed is sodium mesoperrhenate, Na_3ReO_5 . As this compound is readily decomposed by water into sodium perrhenate and sodium hydroxide, so that on reheating the yellow mesoperrhenate can again be formed, it seems probable that the yellow bead formed in this test owes its color to the formation of sodium mesoperrhenate.

When present to a predominating extent, manganese hides the color reactions produced by rhenium in the bead. The presence of the element can be established in mixtures, provided the manganese content is less than 50 per cent of the sample, by heating the bead in the reducing flame of the Bunsen burner, or preferably that of the blowpipe flame. Under these conditions the green manganate compound is not formed, thereby permitting the observation of the yellow color due to the rhenium compound, which is formed in both the oxidizing and reducing flames.

Of the elements which form colored melts with sodium carbonate, only chromium is apt to be mistaken for rhenium. The yellow bead formed by sodium chromate can be differentiated from that formed by rhenium in that the color imparted by the latter is not permanent and fades shortly after its formation. The compounds of tungsten and molybdenum do not interfere with the color reactions of rhenium in the

sodium carbonate bead, as in the presence of this flux they form colorless melts. Molybdic acid imparts a transitory black color to the bead, which disappears as the bead melts and remains colorless on cooling. The yellow coloration due to rhenium can plainly be observed with samples of sodium tungstate and molybdate that contain 1 per cent or more of potassium perrrhenate.

Sensitivity of the Reaction

The characteristic color changes are readily discernible when 1 mg. of potassium perrrhenate is fused into a bead of sodium carbonate weighing 30 mg. With smaller quantities, the initial black coloration is not visible, but the yellow color of the bead can be observed, though the transformation to the colorless stage is much more rapid, as can be seen from Table I.

To establish the minimum quantity of rhenium that can be detected in the bead, calibrated platinum spirals were dipped into solutions of known rhenium content, and the solvent was carefully evaporated by holding the wire about 5 cm. (2 inches) above a microflame. This process deposited on the wire rhenium salts whose weight could be approximated from the concentration of the solution and the capacity of the spiral. When the evaporation was completed the coil was dipped into sifted anhydrous sodium carbonate and heated in a small Bunsen flame until the salt fused.

The spirals are conveniently made by winding several turns of No. 30 platinum wire on a glass rod or other circular form 1 to 2 mm. in diameter and mounting the coil in a glass rod. The spiral is calibrated by dipping the clean wire while hot in distilled water and measuring its increase in weight. The volume of water or solution picked up by the coil varies with the number of turns and will remain constant, even after many operations, provided the wire is kept clean and the sodium carbonate is removed by solution in dilute hydrochloric acid. Repeated tests on a spiral having a capacity of 0.0033 cc. did not show a greater variation in volume than 5 per cent. This method of securing minute weighed samples was first described by Truchot for use in the study of flame spectra (8).

The described method of bead formation was adopted, in preference to the standard procedure of placing the sample on a fused bead, because its use minimizes the loss of material during weighing and as a result of decrepitation in the flame. The method has the further advantage that by building the bead with successive additions of sodium carbonate, traces of a metal left on the wire by the evaporation of the solution impart a deep color to the initial minute bead, thereby rendering detection more certain. The sodium carbonate is sifted so as to avoid rubbing off any of the sample deposited on the wire.

Observations were made first on a solution of pure rhenium metals, standardized by dissolving a weighed quantity of the element in 8 *M* nitric acid and neutralizing the excess acid by the addition of sodium carbonate, and checked by a second solution containing potassium perrrhenate. The results recorded in Table I show that a minimum of 0.015 mg. of rhenium can be detected in the absence of other heavy metals through the formation of a yellow bead and the slow disappearance of its color.

TABLE I. DETECTION OF RHENIUM IN SODIUM CARBONATE BEAD

Concn. of Standard Solution Mg./cc.	Volume Cc.	Rhenium Mg.	Color of 10-Mg. Na ₂ CO ₃ Bead	Persistence Sec.
50 Re	0.0033	0.165	Deep yellow	65
10 Re	0.0033	0.033	Yellow	15
5 Re	0.0031	0.016	Faint yellow	10
15.3 KReO ₄	0.0033	0.030	Yellow	15
7.6 KReO ₄	0.0033	0.015	Faint yellow	10
12 KReO ₄	0.0008	0.006	Faint yellow ^a	15

^a Color visible only in a 2-mg. Na₂CO₃ bead.

Similar observations were made with manganese salts in order to obtain data for a comparison of the relative sensitivity of the bead test for the two metals. Table II reveals that, in the absence of other metals, 0.0008 mg. of manganese can be detected in a bead of sodium carbonate weighing 10

mg. That the limit for rhenium, 0.015 mg., is not of the same order of magnitude can be attributed to two factors: (1) that the transformation to the mesoperrhenate in the sodium carbonate melt is not quantitative, and (2) that the eye is more sensitive to green light than to yellow.

TABLE II. DETECTION OF MANGANESE IN SODIUM CARBONATE BEAD

Concn. of Standard Solution Mg./cc.	Volume Cc.	Manganese Mg.	Color of 10-Mg. Na ₂ CO ₃ Bead
2.94 KMnO ₄	0.0034	0.0035	Emerald green
1.47 KMnO ₄	0.0033	0.0017	Green
0.74 KMnO ₄	0.0033	0.0008	Grayish green
0.37 KMnO ₄	0.0034	0.0004	Very faint green ^a
3.00 MnSO ₄	0.0054	0.0060	Deep green
0.30 MnSO ₄	0.0078	0.0009	Grayish green
0.30 MnSO ₄	0.0033	0.0004	Very faint green ^a

^a Color visible only in a 2-mg. Na₂CO₃ bead.

Tests were made on the detection of minute quantities of rhenium in the presence of the other elements with which it is commonly associated. It was found that in a mixture of 1 part of manganese and 3 parts of rhenium the manganese did not interfere with the detection of 0.05 to 0.1 mg. of rhenium provided the bead was heated in the reducing flame. Also, 0.025 mg. of rhenium can be detected in a 3-mg. sample of either sodium tungstate or molybdate. A single crystal of cesium perrrhenate, as formed under the conditions of the microscopic test for rhenium (1), transferred to a platinum loop and fused with sodium carbonate, gave a yellow bead the color of which persisted for 0.5 minute.

The bead test for rhenium cannot be applied directly to mineral specimens, as even its richest ore, molybdenum glance, seldom contains more than 0.004 mg. of the element per gram (6). The reaction is serviceable in confirming the presence of the metal in the salts crystallized for the microscopic identification of the element, such as cesium and rubidium perrrhenates (1) or cesium iodorhenate (5), and in testing concentrates obtained by analytical processes in which the rhenium is systematically separated from the other elements (4).

Summary

Rhenium can be distinguished from the other elements by the formation of a transitory yellow sodium carbonate bead. The reaction is observable with 0.015 mg. of the metal when the bead is heated in either the oxidizing or the reducing flame, and is not interfered with by the presence of tungstates or molybdates. The test can be applied in the presence of small quantities of manganese by heating the bead in the reducing flame.

Acknowledgment

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Rotenone Determination by Colorimetric Methods

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JONES and Smith (2), realizing the necessity for a sensitive colorimetric test for rotenone, modified the Durham qualitative reaction in an attempt to render the blue color more lasting. The modification, although a sensitive qualitative test, failed to make the color permanent enough for quantitative work. Gross and Smith (1) discovered a red color reaction which they developed into an accurate colorimetric test, but the test was limited to rotenone in acetone solution. Because of the restriction to acetone solution, difficulties were encountered in applying this test to liquid insecticides having refined kerosene bases. The Jones-Smith-Durham test was found useful for detecting rotenone in some liquid insecticides but it failed in several cases when rotenone was known to be present. One substance which interfered with this test was the oil of sassafras.

In the search for a more universal test, the authors found that rotenone in the presence of hydrochloric acid and certain phenols developed color reactions in certain organic solvents. These reactions varied from violet-red to deep blue in color, depending upon the solvent and phenol selected. The organic solvents used were chloroform, ethylene dichloride, carbon tetrachloride, ether, alcohol, and acetone. Phenol and some of the homologs of phenol, such as guaiacol and thymol, also reacted similarly in the solvents named. Small amounts of hydrogen peroxide, nitric acid, and light exerted a marked influence in accelerating the reaction. Isorotenone gave a blue color. Acetylrotenone gave no characteristic color within an hour, but upon standing for several hours a blue-violet color developed.

The advantages of the tests developed over the older methods are its increased sensitivity, making possible an accurate quantitative test satisfactory within the limits stated, and the fact that substances usually found in insecticides do not interfere with the reaction. Some samples of commercial rotenone gave results approximately 15 per cent higher than the known rotenone content. Gross and Smith (1) obtained similar results with their test, which they attributed to the presence of leguelin or some unidentified compounds. The difference in color observed in the detection of rotenone and certain rotenone derivatives may be used as a future basis for investigation in differentiating such substances, as well as serving as an identity test upon comparison with known standards.

A qualitative and two quantitative tests were developed which were not interfered with by substances usually found in proprietary liquid insecticides containing extracts of pyrethrum flowers, aliphatic thiocyanates (Lethane), or oil of sassafras.

The following qualitative test is sensitive to 0.01 mg. of rotenone per ml.:

Dilute 1 to 2 ml. of the insecticide or solution containing rotenone to 5 ml. with chloroform. Add 5 ml. of a chloroform solution of thymol (10 grams of thymol to 100 ml. of chloroform). Add 3 ml. of a nitric acid-hydrochloric acid mixture (0.2 ml. of

concentrated nitric acid to 100 ml. of concentrated hydrochloric acid). Agitate for about 30 seconds. A bluish green to blue color appears when rotenone is present. The color usually appears in from 30 seconds to 2 minutes and deepens on standing. In the presence of the yellow coloring matter of pyrethrum flowers and of derris extract, the color is green and turns upon standing to a bluish green and finally to blue.

Two quantitative tests were developed. No. 1 can be applied to almost colorless liquid insecticides, such as those which contain rotenone and aliphatic thiocyanates (Lethane). If the insecticide base is a refined kerosene, an amount of refined kerosene equal to the amount of liquid insecticides used in the test must be added to the standards.

TEST 1. To 10 ml. of a chloroform solution containing from about 0.05 to 2.5 mg. of rotenone per ml. in a glass-stoppered cylinder, add 10 ml. of a chloroform solution of thymol (10 grams of thymol to 100 ml. of chloroform) and 2 ml. of a reagent made by adding 2.5 ml. of 3 per cent hydrogen peroxide to 100 ml. of concentrated hydrochloric acid. Agitate for 1 minute, loosen the glass stopper, and expose the cylinder to the intense radiation of a quartz mercury vapor lamp having a minimum output of 1000 microwatts per square centimeter in the field of exposure. (The use of bright sunlight produced similar results in approximately 3 hours.) A greenish blue color begins to appear in the chloroform layer in about 15 minutes. At the end of 30 minutes, compare with standards containing known quantities of pure rotenone prepared at the same time in the same manner. When the rotenone sample is not in solution in a hydrocarbon base, concentrated hydrochloric acid may be used in place of the reagent described.

TEST 2. To 5 ml. of an acetone solution containing from 0.1 to 2.0 mg. of rotenone per ml. in a glass-stoppered cylinder, add 5 ml. of an acetone solution of thymol (10 grams of thymol to 100 ml. of acetone), 0.1 ml. of 3 per cent hydrogen peroxide, and 5 ml. of concentrated hydrochloric acid. A reddish violet color appears within 30 seconds. After 1 minute place the glass container in a water bath at about 20° C., and at the end of 20 minutes compare with rotenone standards, similarly prepared, at the same time.

When the liquid insecticide contains pyrethrum and rotenone (not derris extract) in a refined kerosene base, proceed as follows:

Prepare an extract of pyrethrum with refined kerosene. (Add 1.8 kg., 4 pounds, of pyrethrum to 3.785 liters, 1 gallon, of refined kerosene and allow to stand at least 2 days.) Filter and preserve. Match the color of the insecticide, approximately, with the extract by diluting with refined kerosene. Prepare a chloroform solution of rotenone of suitable concentration. Use the diluted pyrethrum extract and rotenone solution in preparing the standards using the same amount of extract in the standards as insecticide used in the test. Proceed as in quantitative test No. 1.

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Determination of Iron in Sea Water

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CONSIDERABLE interest attaches to the heavy metals present in small amounts in sea water. Of these, iron is particularly important, for there is little doubt but that it may be a limiting factor in the growth of certain organisms. Thompson, Bremner, and Jamieson (3) reviewed the literature on this subject and proposed a method for the determination of total iron in the water.

Any study of the availability of iron must involve its separation into the several possible forms of combination. Thompson and Bremner later (1) modified their method and determined both "soluble" and "total" iron in a number of samples of water. The present paper describes an attempt to determine the concentration of "free dissolved ferrous and ferric ions," and since a somewhat different method of analysis is used the results are not strictly comparable with those of Thompson and Bremner, who evaporated filtered samples with sulfuric acid to eliminate interfering substances such as fluoride and organic matter, and then determined iron colorimetrically with thiocyanate, extracting the color with isoamyl alcohol.

The method here described depends primarily upon the precipitation of iron as sulfide. The results therefore include iron in all forms of combination yielding ferrous ions in the concentrations demanded by the solubility product of ferrous sulfide. Ferric ions are also included, owing to the reducing action of the sulfide ion in the concentrations used. Admittedly, organic matter interferes with the precipitation, but whether this actually occurs in sea water and, if so, how much of the iron is held in such organic combination, is outside the present discussion.

Much of the early work on heavy metals in sea water was based upon their precipitation by sulfide, but unless some method of concentration is used the removal is incomplete in such high dilutions. However, the fortunate presence of magnesium in relatively large amounts makes it possible to use a process of co-precipitation, the extremely small quantities of ferrous sulfide resulting from the addition of alkaline sulfide being carried down quantitatively by the larger amount of basic magnesium salts simultaneously formed. The iron is brought into solution again in small volume, oxidized, and finally estimated colorimetrically with thiocyanate.

A serious difficulty with this latter reaction has always been the instability of the colored compound in water solution. While trying various methods of extraction it was observed that ethylene glycol monobutyl ether, which is a moderately good extractive, will, when dissolved in the solution in small amounts, stabilize the color reaction and retard the fading long enough to permit colorimetric comparison in the water solution without extraction by any organic solvent.

Method Used

A 500-ml. sample of sea water is filtered through a Seitz filter and transferred to a 1-liter Erlenmeyer flask. Five milliliters of ammonium sulfide reagent are added and the solution is brought to boiling for a few moments. A fine magnesium precipitate should form, which settles quickly on standing. If the precipitate fails to appear, the solution is not sufficiently alkaline, and a small amount of ammonium hydroxide (ordinarily not more than 5 ml.) should be added and the boiling repeated. The precipitate is filtered on a small paper filter in a Gooch crucible, under gentle suction. After washing, it is dissolved in 20 ml. of dilute hydrochloric acid (approximately 2.5*N*) and the solution boiled to remove hydrogen sulfide. Then 2 ml. of bromine water are

added and the excess bromine is boiled off. When the solution has cooled, 5 ml. of concentrated hydrochloric acid are added, and the solution is made alkaline with concentrated ammonium hydroxide. In this way iron is precipitated, with only small traces of magnesium. The precipitate is filtered off on a small Whatman paper (No. 42) and dissolved by running 20 ml. of 2.5*N* hydrochloric acid through the filter. The filtrate is caught in a 100-ml. Nessler tube and made up to the mark. Then 2 ml. of ethylene glycol monobutyl ether and 10 ml. of a 10 per cent solution of potassium thiocyanate are added and the contents of the tube mixed by covering the ground end of the tube with a glass plate and inverting. The color is compared with a set of standards in similar tubes. These are prepared by adding 5 ml. of concentrated hydrochloric acid and the desired amount of standard iron solution (0.002, 0.005, 0.01, 0.015, 0.02 mg. of iron as ferric alum) to Nessler tubes and treating with potassium thiocyanate and the ether as before. The colors will remain permanent for an hour or more.

If preferred, the color comparison may be carried out in a long-tube colorimeter, which makes closer differentiation possible than with the use of Nessler tubes, but it is very doubtful whether in the long run the results are any more accurate.

Occasionally samples of c. p. hydrochloric acid and ammonium hydroxide are found which are practically iron-free. If not, the reagents may be made by redistilling the purified gases into pure water. The ammonium sulfide reagent is made by running hydrogen sulfide into iron-free ammonium hydroxide through a purification train consisting of a wash-bottle and a 120-cm. (4-ft.) tube packed with glass wool.

The bromine water was tested daily for the presence of iron taken from the glass. The greatest source of error was found in the filter paper. This was minimized by soaking all filter paper and pads in 1 to 1 hydrochloric acid and washing carefully.

BLANKS. In the early stages of the work, before reagents were adequately purified, blank values from 0.005 to 0.0065 mg. were found. Later this was consistently lowered to 0.002 to 0.004 mg. Each reagent was separately tested as a possible source of iron, with the following results, when reduced to the basis of a single determination:

	Mg.
Bromine	0.0008
(NH ₄) ₂ S	0.0010
HCl	0.0026
NH ₄ OH	0.0010
Total	0.0054

DUPLICATE DETERMINATIONS. The following pairs of results were obtained at various times from duplicate samples, independently precipitated and treated:

Mg. of Iron Found							
0.012	0.005	0.018	0.017	0.015	0.023	0.005	0.015
0.010	0.004	0.017	0.019	0.015	0.021	0.004	0.015
0.0044	0.0077	0.0052	(comparison made in colorimeter)				
0.0045	0.0073	0.0053					

Recovery of Added Iron

The test of the adequacy of the method is in the completeness with which added quantities of iron may be recovered. Known amounts of iron, in the order of magnitude which might be expected to be present in the original water, were added to sea-water samples with the results shown in Table I. The iron added was in the form of ferric ammonium sulfate. It is evident from the completeness of the recovery that ferric iron is completely reduced to ferrous by the sulfide ion, before precipitation of ferrous sulfide.

TABLE I. RECOVERY OF ADDED IRON

Before Adding Iron Mg.	Iron Added Mg.	Found after Adding Iron Mg.	Iron Recovered Mg.	
0.01	0.02	0.025	0.015	
0.01	0.03	0.04	0.03	
0.015	0.02	0.04	0.025	
0.015	0.02	0.035	0.02	
0.012	0.03	0.042	0.03	
0.01	0.02	0.035	0.015	
0.001	0.005	0.0062	0.0052	Comparison in colorimeter
0.002	0.005	0.0068	0.0048	
0.015	0.010	0.025	0.010	High blank (0.007 mg.) Reagents and paper impure
0.017	0.010	0.025	0.008	
0.010	0.010	0.023	0.013	
0.012	0.010	0.023	0.011	
0.010	0.010	0.021	0.011	
0.005	0.010	0.015	0.010	
0.004	0.010	0.015	0.011	
0.007	0.010	0.015	0.008	
0.005	0.010	0.017	0.012	
0.008	0.010	0.017	0.009	
0.008	0.010	0.018	0.010	
0.005	0.010	0.015	0.010	
0.004	0.010	0.015	0.011	

TABLE II. DUPLICATE SAMPLES FILTERED IN DIFFERENT WAYS

(Mg. of iron found)					
No. 42 paper	0.0045	0.017	0.025	0.017	Comparison in colorimeter
Seitz filter	0.002	0.010	0.023	0.010	
No. 42 paper	0.004	0.003	0.0009	0.0004	
Seitz filter	0.0003	0.0003	0.0004	0.0000	

TABLE III. INFLUENCE OF FLUORIDE

Fe in Original Water Mg.	Fluoride Added to Sample Mg.	Iron Found Mg.
0.018	0.25	0.017
0.017	0.25	0.019
0.012	0.25	0.010
0.012	0.50	0.011
0.012	0.75	0.013
0.016	0.12	0.015
0.016	0.50	0.021
0.016	1.00	0.015

Filtration

Obviously, if the original water is not filtered to remove suspended matter results will be high, owing to iron contained in such material, even though the subsequent treatment is not vigorous enough to oxidize or decompose completely the organic iron compounds contained in diatoms, etc. This is borne out by the results shown from Station 1731, the samples from which were not filtered, and which are higher than any others. The results given in Table II, comparing duplicate samples, one of which had been filtered through No. 42 filter paper and the other through a Seitz filter, indicate that water treated in the latter way is more completely free from iron-bearing suspended matter. The samples in which Thompson and Bremner (1) determined "soluble iron" were filtered through No. 42 paper, which may account for their slightly higher results.

The varying results following different methods of filtration are evidently due not to iron dissolved from the filter

material, but rather to the varying efficiency of different filtration technics in the removal of very fine suspended matter, bacteria, or other microorganisms containing iron. The greater portion of the total iron of the water is in suspension.

Influence of Fluoride

Thompson, Bremner, and Jamieson mention the possible occurrence of iron in the form of a ferrifluoride complex, which inactivates the iron as far as the thiocyanate reaction is concerned. Although this may be true, the presence of fluoride has no influence on the determination and recovery of iron by the present method. The amount of fluoride in the water should be sufficient to form such complex ions with much more than the iron already present; nevertheless, added iron is recovered quantitatively. Furthermore, fluoride was added to water samples containing small amounts of iron, which were precipitated and determined both before and after the addition of fluoride. The results shown in Table III es-

TABLE IV. IRON IN SEA WATER

Location	Depth M.	Tem- perature ° C.	Sal- inity 0/00	Iron Mg./cu. m.	Location	Depth M.	Tem- perature ° C.	Sal- inity 0/00	Iron Mg./cu. m.
Station 1731 38° 06' N., 68° 54' W.	0	28.20	36.02	19 Not	Station 2220 42° 17' N., 69° 36' W. (Gulf of Maine)	0	13.96	31.73	6
	50	26.81	36.00	41 filtered		20	13.88	31.95	0
	100	23.42	36.40	30 Compare		40	4.09	32.64	0
	150	20.95	36.58	16 with fol-		60	3.66	32.79	0
	200	18.65	36.42	16 lowing		80	3.65	32.92	4
	860	4.71	34.96	15 stations		120	3.98	33.25	4
	1685	3.48	34.94	8 Filtered		175	6.07	33.96	18 (?)
Station 1732 37° 21' N., 68° 31' W.	0	27.67	35.90	13		200	6.48	34.12	0
	1370	4.65	34.96	4	Station 2224 43° 12' N., 69° 18' W. (Gulf of Maine)	0	12.68	32.00	0
	2390	3.42	34.96	6		40	5.57	32.60	0
	2830	3.11	34.97	10		80	4.15	32.80	0
	3830	2.50	34.87	8		175	3.94	33.22	0
Station 1734 36° 27' N., 68° 38' W.	0	25.64	36.00	9	Station 2227 42° 15' N., 67° 16' W. (Gulf of Maine)	0	12.56	32.28	4
	50	21.03	36.56	2		40	5.01	32.82	0
	87	19.75	36.56	3		80	4.78	33.12	0
	175	18.55	36.51	5		175	5.39	33.80	0
	365	17.96	35.53	5	Station 2228 41° 57' N., 67° 06' W. (Gulf of Maine)	0	9.63	32.52	0
	550	17.00	36.35	6		30	9.59	32.52	0
	730	14.43	35.90	1		50	9.61	32.52	0
	900	10.21	35.34	4	Surface Samples near Woods Hole				
	1330	4.82	34.96	8	Woods Hole Harbor (8/6/34)				6
	1550	4.08	34.97	2		(8/8/34)			8
	2440	3.45	34.96	2		(8/28/34)			7
Station 2450 39° 37' N., 69° 57' W.	0	22.23	33.15	10		(8/28/35)			3
	50	9.35	34.39	4	Woods Hole Eel Pond				0
	500	5.08	34.96	6	Mouth of Great Pond				4
	1000	3.88	34.96	14	Head of Waquoit Bay				10
	2200	3.29	34.96	8	Tarpaulin Cove				6
Station 2458 5° 54' N., 67° 47' W.	0	27.8	36.26	6	Buzzards Bay, K-1				3
	100	22.84	36.47	6	Buzzards Bay, K-2				0
	200	18.93	36.56	6	Vineyard Sound, L-1				0
	500	17.97	36.49	12	Vineyard Sound, L-2				0
	1000	10.2	35.25	14					
	2500	3.37	34.90	8					

establish the fact that fluoride in several times the normal concentration has no influence on the determination of iron by this method.

Iron in Sea Water

Sea-water samples from a number of places within cruising distance of Woods Hole were analyzed by the above procedure. The results in Table IV show that there is a small but significant amount of free inorganic iron—i. e., iron precipitable as sulfide—generally present in the water. The concentration is seldom more than 10 mg. per cubic meter, or ten parts per billion. This is about one-quarter to one-twentieth of the amount of total iron found in the waters of the Puget Sound area, by the authors mentioned.

The figures of Thompson and Bremner (2) for "soluble iron" are also somewhat higher than those shown here, except in the case of their one deep, off-shore station, where results were much the same as at Stations 1732 and 1734. Their discovery of a maximum iron concentration at 1000 to 1200 meters seems to have its counterpart here, too, at Stations 2450, 2458, and possibly 1734, although at the first of these, at least, it does not coincide with the depth of minimum

oxygen concentration, which the above authors think is related to it.

The water is occasionally free of this form of iron, especially on the surface near the shore, and sometimes at other depths, as at Stations 2220–28 in the Gulf of Maine. Whether this is entirely due to utilization of the metal biologically, or whether this same process is the cause of the vertical differences in concentration (as was shown to be the case with total iron, 3), cannot be decided conclusively from the present data. At any rate, the growth of diatoms would seem to depend principally upon other forms of iron than those responding to this method of analysis. Presumably these are in the nature of organic or nondissociable compounds.

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Determination of Reducing Sugars and Sucrose in Plant Materials

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Details are given for the clarification of extracted plant materials and for determining reducing sugars.

The reducing sugars are oxidized with alkaline potassium ferricyanide; the ferrocyanide formed in the reaction is titrated in acid solution with ceric sulfate, which oxidizes the ferrocyanide back to ferricyanide, giving a measure of the reducing sugars present. The indicator used for the titration is *o*-phenanthroline ferrous sulfate.

Using five different dry plant materials and squash sap, the results obtained were from 0 to about 5 per cent higher by this method than by the Munson-Walker method. The method is rapid and convenient, and covers a wide range of the sugar contents encountered in plants.

THE Munson-Walker method (5), most widely used for determination of reducing sugars in plants, gives satisfactory results when samples containing large amounts of sugars are used. Reliable results, however, cannot be obtained when the samples to be analyzed contain small amounts of sugar. The Committee on Methods of Chemical Analysis of the American Society of Plant Physiologists (1) referring to this method states, "As a general rule, reductions giving less than 20 mg. of copper should not be weighed directly, and even at this figure the percentage error is high."

The volumetric methods used at present for the determination of sugars in plants are not satisfactory. The writer, using two known reactions, developed a method which gives satisfactory results when reducing sugars are determined in plant tissues and saps. The reaction between the ferricyanide and reducing sugars was first suggested by Gentele (3). Furman and Evans (2) have shown that ferrocyanide can be oxidized quantitatively by ceric sulfate. Whitmoyer (6) was first to utilize these reactions and devised a microchemical method to determine pure glucose, fructose, and invert sugar for amounts between 0.5 and 2.0 mg.

In the present method, precise results can be obtained with samples containing between 1.0 and 10.0 mg. of reducing sugars. The method is short, the solutions are stable, and a sharp end point is obtained in the titration.

Materials and Solutions

INDICATOR. A 0.025 *M* solution of *o*-phenanthroline ferrous sulfate was used as an indicator. It was made by dissolving 0.695 gram of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water; 1.485 grams of *o*-phenanthroline monohydrate were added and stirred until all dissolved, giving a dark red solution, which was then made up to 100 cc. volume. Two drops of the indicator were used in each determination. Care should be taken to use exactly the same amount of indicator in each determination, because the ferrous sulfate in the indicator is oxidized by the ceric ion. A blank should therefore be run on the indicator used. The blank was found to be 0.30 cc. when a 0.0135 *M* ceric sulfate solution and 2 drops of the indicator were used. The end point was a sharp change from orange-brown to pale green. The indicator was obtained from the G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio.

CERIC SULFATE. The ceric sulfate was obtained from the same source as the indicator and standardized against 0.1 *N* ferrous sulfate as follows:

The ferrous sulfate was first standardized against 0.1 *N* potassium dichromate by dissolving 6.95 grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water to which 20 cc. of 1 to 1 sulfuric acid had been added and diluted to 250 cc. Twenty-five cubic centimeters of the approximately 0.1 *N* ferrous sulfate were transferred with a calibrated pipet into a 300-cc. Erlenmeyer flask to which 15 cc. of 1 to 1 sulfuric acid and 25 cc. of water were added. One drop of the *o*-phenanthroline ferrous sulfate was added and titrated against standard 0.1 *N* potassium dichromate until the pink solution turned bluish green. It took 27.5 cc. of the 0.1 *N* potassium dichromate to neutralize 25 cc. of the ferrous sulfate. The concentration of the ferrous sulfate was therefore 0.11 *N*.

To 8.3063 grams of ceric sulfate dissolved in water, 75 cc. of 1 to 1 sulfuric acid were added and the solution was diluted to 250 cc. (The molecular weight of ceric sulfate being 332.25, this should be a 0.1 *N* solution.) A 25-cc. aliquot of this ceric sulfate solution was transferred to a 300-cc. Erlenmeyer flask. Fifteen cubic centimeters of 1 to 1 sulfuric acid, 25 cc. of water, and one drop of the indicator were added, and the solution was titrated with the standard ferrous sulfate. The change from the colorless or slightly green to orange-pink was taken as the end point. To neutralize 25 cc. of ceric sulfate 12.75 cc. were required. The concentration of the ceric sulfate was 0.0539 *N*, which is 53.9 per cent purity of the ceric sulfate used.

The ceric sulfate obtained from the G. Frederick Smith Chemical Company is not completely anhydrous and contains other rare earth metals. However, as the ceric ion is the only quadrivalent ion effective in the oxidation, the other metals do not interfere.

A dilute ceric sulfate solution suitable for use in sugar analysis was made by placing 8.3 grams of the ceric sulfate in about 500 cc. of water to which 100 cc. of 1 to 1 sulfuric acid had been added and diluting to 1 liter at room temperature.

This dilute ceric sulfate solution was standardized against the standard 0.11 *N* ferrous sulfate solution in the following manner:

A 2-cc. aliquot of the ferrous sulfate solution was transferred to a 300-cc. Erlenmeyer flask and 15 cc. of 1 to 1 sulfuric acid, 25 cc. of water, and one drop of the indicator *o*-phenanthroline ferrous sulfate were added. The solution was then titrated with the dilute ceric sulfate solution until the pink color disappeared, changing to bluish green and then becoming colorless. Two cubic centimeters of the 0.11 *N* ferrous sulfate required 16.25 cc. of the ceric sulfate. The concentration of the ceric sulfate solution was therefore 0.0135 *N*. The solution was very stable; its concentration did not change after standing for 3 months.

The ceric sulfate solution could also be standardized by the method of Willard and Young (7).

ALKALINE POTASSIUM FERRICYANIDE. A mixture of 4 grams of potassium ferricyanide and 24 grams of sodium carbonate was used to make up 1 liter of solution. The container of this solution was painted black and when not in use was kept in the dark. Under these conditions the alkaline potassium ferricyanide solution remained stable during 6 weeks.

STANDARDIZATION OF CERIC SULFATE AGAINST GLUCOSE. An aliquot of 1, 2, 5, and 10 cc. of pure 1 per cent anhydrous glucose, $[\alpha]_D^{25}$ 52.5, was placed in each of four 100-cc. volumetric flasks and made up to volume. A 10-cc. aliquot from each of these flasks, containing 1, 2, 5, and 10 mg. of glucose, was placed in a 200-cc. Erlenmeyer flask, and 25 cc. of alkaline potassium ferricyanide were added to each flask. The flasks with their contents were placed on the steam bath, so that they were immersed about one-third. After exactly 10 minutes the flasks were removed and cooled to room temperature by immersing them in running water for a few minutes, 10 cc. of 5 *N* sulfuric acid were added, and the flasks were well shaken. Two drops of the indicator, *o*-phenanthroline ferrous sulfate, were added and the solution was titrated with the 0.0135 *N* ceric sulfate solution.

The amount of ceric sulfate used, after subtracting the blank due to the indicator, was directly proportional to the amount of glucose taken. One milligram of glucose was equivalent to 2.14 cc. of 0.0135 *N* ceric sulfate.

Description of Method

CLARIFICATION OF PLANT EXTRACT. The plant extract should be clarified so that it is devoid of any coloring matter

and must be water-clear. Any organic coloring matter present in the solution is, apparently, oxidized by the ceric ion and high results are obtained.

A water-clear plant extract can be obtained if the clarification is carried out in a small volume and a small amount of charcoal (carboraffin) is added. The plant material, after extraction with 80 per cent alcohol and evaporation of the alcohol, is concentrated to not more than 10 cc. Five cubic centimeters of saturated neutral lead acetate are added and the excess of lead is removed with 10 cc. of saturated disodium phosphate. (The use of oxalate for deleading should be avoided because of its oxidation by the ceric sulfate.) Carboraffin (0.3 gram) is added and the mixture is allowed to stand with occasional shaking for half an hour. It is then filtered on a small Büchner funnel containing a thin layer of talc on a filter paper, prepared as follows:

Fifty grams of talc powder are shaken with 500 cc. of water until a uniform suspension results. About 25 cc. of the suspension are poured through a small Büchner funnel supplied with a wet 5.5-cm. filter paper and a 250-cc. suction flask, using little suction. The uniformly thin layer of talc is sucked free of liquid, washed with a little water, and sucked free of liquid again. The water in the suction flask is poured out and the flask rinsed with water. Full suction is then applied and the plant extract containing the clarifying agents is filtered through the dry talc filter. The precipitate on the filter is finally washed with water.

HYDROLYSIS OF SUCROSE IN PLANT EXTRACT. A 50-cc. portion of the clarified plant extract was taken and one or two drops of methyl red were added. The solution, which was slightly basic because of the excess of disodium phosphate used in the clarification, was neutralized with a few drops of 10 per cent acetic acid to bring to the acid color of methyl red. The pH of the solution was 4.9. Two to four drops of a 1 per cent solution of Wallerstein invertase scales were added. (The invertase was obtained from The Nulomoline Co., 111 Wall St., New York, N. Y.) It is necessary to run a blank on this invertase, as it has a slight reducing power. The solution was allowed to stand for 2 hours at 28° or overnight at room temperature, made up to volume, and 10-cc. aliquots were used for the determination of reducing sugars. The acid hydrolysis of sucrose as used by Lehmann (4) was also found to be satisfactory. Fifty cubic centimeters of the clarified plant extract were transferred to a 200-cc. Erlenmeyer flask, heated to 70° for 10 minutes, then cooled rapidly in running water, and sufficient 15 per cent sodium hydroxide was added to neutralize to phenolphthalein. The actual amount of alkali needed was determined on a duplicate sample, so that no indicator was added to the solution to be analyzed. The neutralized solution was then made up to 100-cc. volume and 10-cc. aliquots were used for the determination of reducing sugars.

PROCEDURE. The following method was adopted for the determination of reducing sugars and sucrose:

One to two grams of dry material were weighed into glass thimbles provided with sintered glass porous bottoms and placed in Soxhlet extractors. One hundred and twenty-five cubic centimeters of 80 per cent alcohol were added to each of the 300-cc. Erlenmeyer flasks, connected with the extractors to the reflux condensers, and extracted for 6 hours. The flasks with the alcoholic extracts were placed on a steam bath, evaporated to about 10 cc., then cooled to room temperature, and cleared with 5 cc. of saturated neutral lead acetate. The excess lead was removed with 10 cc. of saturated disodium phosphate, 0.3 gram of charcoal was added, and the mixture was allowed to stand, with frequent shaking, for 30 minutes. The precipitate with the charcoal was then filtered on a small Büchner funnel supplied with a thin talc layer on a filter paper prepared as described above. The flasks were rinsed with cold water and the final washing of the precipitate on the Büchner was made with warm water. The clear solutions were diluted in volumetric flasks to 100 or 200 cc.

Aliquots of 10 cc. were transferred to 200-cc. Erlenmeyer flasks, 25 cc. of alkaline ferricyanide were added, and the flasks were heated on the steam bath, cooled, acidified, and titrated with 0.0135 *N* ceric sulfate as described above.

The 10-cc. aliquots should not contain more than 10 mg. of reducing sugar. If more than this amount is present, the

ferricyanide used is not sufficient to oxidize all of the reducing sugars. This can easily be detected by the disappearance of the yellow color of the ferricyanide, the solution becoming colorless after being heated on the steam bath. In that case the sugar solution should be diluted to a suitable volume.

A standard 25-cc. buret was used for the titration with the ceric sulfate. For blank determinations and for samples containing not more than 4 mg. of reducing sugar, a 10-cc. buret calibrated to 0.05 cc. was used.

When plant saps which did not contain much chlorophyll and other coloring matter were analyzed, 5-cc. samples were taken and clarified as in the case of the extracted plant material but were not filtered with suction on a Büchner funnel. Instead, they were filtered on an ordinary funnel and filter paper directly into 100-cc. volumetric flasks.

The sucrose was determined as follows: 50-cc. aliquots of the clarified plant extracts were placed in 100-cc. volumetric flasks and one or two drops of methyl red were added. The solution was then neutralized with a few drops of 10 per cent acetic acid to bring to the acid color of methyl red. Four drops of a 1 per cent solution of Wallerstein invertase scales were added and the flasks were placed at 28° for 2 hours or left overnight at room temperature. The flasks were then diluted to volume; 10-cc. aliquots were taken and determined as in the case of reducing sugars.

A blank was simultaneously run with water and the same dose of invertase using 2 drops of the *o*-phenanthroline indicator as in the sugar determinations.

CALCULATION OF RESULTS. If, for example, in determining reducing sugars, a 10-cc. aliquot of the clarified extract from 2 grams of dry material diluted to 200 cc. required 16.2 cc. of the standardized ceric sulfate, the blank being 0.30 cc., the calculation is made as follows:

$$\frac{(16.2 - 0.3) \times 20 \times 100}{2.14 \times 2000} = \text{per cent of reducing sugar}$$

Experimental Results

The titration was 0.30 cc. of 0.0135 *N* ceric sulfate, when 10 cc. of water and 2 drops of the indicator were used.

A blank, substituting water for the plant extract, required 0.30 cc. of 0.0135 *N* ceric sulfate. Since the amounts used in titrating the indicator and the indicator plus reagents were the same, apparently the buffering effect due to the acetate and phosphate has no noticeable effect on the reducing power of the solution.

A blank on the invertase showed a titration of 0.38 cc. of the 0.0135 *N* ceric sulfate.

In order to determine whether any sugar was adsorbed by the lead precipitate, charcoal, and talc, pure glucose was subjected to the same treatment as the plant samples. The results in Table I show a complete recovery of the glucose; hence no sugar was lost in the process of clarification.

TABLE I. EFFECT OF CLEARING ON PURE SUGAR SAMPLES

Glucose Dissolved in 100 Cc. Mg.	Glucose Recovered Mg.	Glucose Recovered %
50.00	50.06	100.1
50.00	50.00	100.0
50.00	49.92	99.8
100.00	99.84	99.8
100.00	100.10	100.1

Different plant materials were analyzed by the volumetric and Munson-Walker methods. The results are shown in Table II. The values for the ten samples determined by the volumetric method were higher by 1.17 to 4.27 per cent than by the Munson-Walker method.

TABLE II. COMPARISON OF VOLUMETRIC WITH MUNSON-WALKER METHOD

(Reducing sugars calculated as glucose)					
Plant Material	Volumetric Method		Munson-Walker Method		Difference
	Glucose	Glucose	Glucose	Glucose	
	per gram	in dry	per gram	in dry	
	of dry	ma-	of dry	ma-	
	material	terial	material	terial	
		%		%	%
Before Hydrolysis					
Swiss chard	30.4	3.04	29.4	2.94	3.40
Cauliflower leaves	34.2	3.42	32.8	3.28	4.27
Sugar cane	86.2	8.62	85.2	8.52	1.17
Sugar beets	57.4	5.74	55.7	5.57	3.05
Sunflower leaves	41.0	4.10	39.4	3.94	4.06
After Hydrolysis					
Swiss chard	57.2	5.72	55.6	5.56	2.88
Cauliflower leaves	83.0	8.30	79.8	7.98	4.01
Sugar cane	158.4	15.84	152.8	15.28	3.67
Sugar beets	115.0	11.50	111.5	11.15	3.14
Sunflower leaves	70.0	7.00	67.7	6.77	3.43

In another experiment 1-gram samples of the same plant material were mixed before extraction with 50 mg. of pure glucose with 80 per cent alcohol, and the reducing sugars were determined by the volumetric method as before. There was a good recovery of glucose added to the samples, as may be seen from Table III.

TABLE III. RECOVERY OF PURE GLUCOSE, USING THE VOLUMETRIC METHOD, WHEN MIXED WITH PLANT MATERIAL

Plant Material	(Reducing values calculated as glucose)			
	Glucose per Gram of Dry Material Mg.	Glucose per Gram of Dry Material after Adding 50.0 Mg. of Glucose Mg.	Glucose Recovered Mg.	Recovery %
Swiss chard	30.4	80.1	49.7	99.4
Cauliflower leaves	34.2	82.8	48.6	97.2
Sugar cane	86.2	137.5	51.3	102.6
Sugar beets	57.4	106.4	49.0	98.0
Sunflower leaves	41.0	91.5	50.5	101.0

Table IV shows the results obtained when expressed squash saps were determined by the volumetric and Munson-Walker methods. The results obtained by the volumetric method in 10 samples run higher from 0 to 4.83 per cent than the Munson-Walker method.

TABLE IV. COMPARISON OF VOLUMETRIC WITH MUNSON-WALKER METHOD WHEN PLANT SAP WAS USED

Volumetric Method	(Reducing sugars calculated as glucose)			
	Volumetric Method		Munson-Walker Method	
	Glucose in 5 cc. of sap Mg.	Glucose in 1 liter of sap Grams	Glucose in 5 cc. of sap Mg.	Glucose in 1 liter of sap Grams
110.0	22.00	105.0	21.00	4.76
61.3	12.26	59.0	11.80	3.90
78.4	15.68	78.4	15.68	0
79.2	15.84	78.5	15.70	0.89
75.4	15.08	73.2	14.64	3.00
88.6	17.72	85.6	16.12	3.51
32.3	6.46	31.4	6.28	2.87
71.7	14.34	68.4	13.20	4.83
67.9	13.58	66.0	13.20	2.88
77.4	15.48	74.6	14.92	3.75

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The Assay of the Platinum Metals

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THE determination of the platinum metal content of the silver bead has always been recognized as exceptionally difficult, because of the similarity of properties of metals of the platinum group, the necessity of working with small quantities of the metals, and the absence of methods for separating and determining such metals as rhodium, iridium, osmium, and ruthenium.

The authors have been engaged in determining the platinum metal content of a certain Canadian mineralized property and consequently were faced with the necessity of devising a method for the complete extraction and determination of the platinum metal group. A search through the literature dating back to the discovery of the metals yielded no method for the analysis of the bead which could be considered at all satisfactory from the point of view of the complete individual separation of the platinum group and of effecting complete solution of such metals as rhodium and iridium when these are present together in the cupelled bead.

Much valuable work has been done on the determination of the individual platinum metals and on restricted separations, such as the separation and determination of platinum and palladium by Krauss and Deneke (9). Paal and Amberger (11) established the foundations for a new method of separation of the platinum metals in the use of the oxides of the metals precipitated in a medium of controlled acidity. Wichers, Gilchrist, and Swanger (12) extended very successfully these and other researches to the complete wet separation of the platinum metals and devised a macroprocedure for their determination, which the authors have found of exceptional value. Their work was not designed to apply to the assay bead containing members of the platinum group, gold, and silver. The authors have made use of this work in an attempt to devise a simple and accurate procedure for the fire assay of the platinum metals. The present report deals with some of the individual problems encountered during the development of the combination method of assay.

Distribution of Palladium

The procedures for parting the silver-platinum metal bead by means of sulfuric acid may be divided into two classes. In the modified parting method, advocated by Graham (8) for routine analysis, an attempt is made to remove the silver from the platinum metal residue. The parting is stopped at the last appearance of gas bubbles, and undoubtedly the amount of palladium dissolved will depend upon the interpretation of the end point. In the second, the bead is parted in boiling sulfuric acid. Fulton and Sharwood (4) state that when the bead is parted by this method palladium is dissolved, leaving the remaining metals in the residue, and that "whether this solution is complete or not has not been demonstrated." In a footnote they mention that "Lodge holds o the contrary."

Beads were made up containing the proportion of platinum metals found in ore concentrates from various localities chosen

A new procedure has been developed for the separation of palladium from silver in sulfuric acid solutions obtained as a result of parting the platinum-silver bead, and for the treatment of iridium and rhodium, which are dissolved by means of a short sodium peroxide fusion in a silver crucible. Palladium is tenaciously retained in the residue left after having parted the bead with sulfuric acid, and hence provision must be made for its extraction from the residue. The effect of dimethylglyoxime on rhodium, iridium, osmium, and ruthenium solutions is shown.

because of the variable ratio of palladium to the rest of the platinum metals. Those chosen contained the following approximate percentages of metals: Ontario concentrates, 78.0 silver, 8.3 platinum, 9.4 palladium, 0.6 rhodium, 0.6 iridium, and 3.0 gold; South African concentrate I, 61.4 platinum, 34.3 palladium, 1.0 iridium, and 2.6 rhodium; South African concentrate II, 83.5 platinum, 9.2 palladium, 0.9 iridium, and 0.8 rhodium. Each bead contained about 12 parts of silver to 1 part of platinum metals.

The bead was flattened and rolled into a cornet, 20 cc. of concentrated sulfuric acid were added, and the whole was boiled for 20 minutes. (The authors have since observed that there is a consistent loss of platinum metals during the flattening of the bead unless extreme precautions are taken. In a forthcoming paper this matter will be discussed more fully.) The sulfuric acid was removed, a second portion of 15 cc. of concentrated sulfuric acid added, and the mixture boiled for 15 minutes in some cases and for 30 minutes in others. The residue was washed thoroughly with hot water and dilute sulfuric acid until the washings showed no test for palladium with dimethylaminobenzilidene rhodanine, as described by Feigl (3). The residue was dissolved in the usual way with aqua regia and the nitric acid removed. When gold was present it was removed by reduction with oxalic acid which also precipitated small amounts of palladium.

The gold was filtered off and the filtrate containing platinum and palladium made up to 30 cc. with hot water. The acidity of this solution was adjusted to pH 4 by means of a filtered 10 per cent solution of sodium bicarbonate and bromophenol blue indicator. Two cubic centimeters of a filtered 10 per cent solution of sodium bromate were added and the solution was boiled for 15 minutes. The addition of the sodium bicarbonate solution was then continued to an acidity of pH 6, using bromocresol purple as indicator. The brown palladium dioxide was filtered through a small filter paper and washed with hot water freshly distilled. (Distilled water which has been exposed to fumes of ammonia or acids will vary considerably from its usual pH of about 6. Particularly in the case of rhodium, the dioxide is carried through the filtering medium as suspended material if the wash water is much more basic than pH 6. In this case the water can be adjusted by addition of dilute sulfuric acid.) The palladium dioxide was dissolved by pouring 4 cc. of a hot hydrochloric acid solution (1 to 1 by volume) through the filter paper and washed with about 30 cc. of hot water. The palladium was precipitated with dimethylglyoxime and filtered through a No. 00 Munktell's 7-cm. filter paper. The washed compound was ignited, reduced, cooled in an atmosphere of carbon dioxide and then air, and finally weighed as metal. When gold was absent the palladium was precipitated from the acid solution of palladium and platinum as the dioxide and then with dimethylglyoxime as described above. The results obtained are given in Table I.

TABLE I. DISTRIBUTION OF PALLADIUM IN BEAD ON PARTING WITH SULFURIC ACID

Sample No.	Type of Concentrate	Palladium Content Mg.	Time of Parting Min.	Residue Mg.
1	Ontario	24.18	20 and 15	1.56
2	Ontario	24.03	20 and 15	1.36
3	Ontario	24.51	20 and 30	0.92
4	Ontario	23.19	20 and 30	1.00
5	South Africa I	18.36	20 and 15	2.21
6	South Africa I	17.85	20 and 30	2.38
7	South Africa II	5.04	20 and 15	0.41
8	South Africa II	4.98	20 and 30	0.00
9	South Africa II	5.14	20 and 30	0.35

Distribution of Platinum, Rhodium, Osmium, and Ruthenium

Throughout these experiments it was observed that when the second parting was continued for 30 minutes, and particularly in those cases not recorded where the parting time was longer, while the amount of palladium present generally decreased, yet appreciable amounts of platinum and rhodium passed into the solution. These facts indicate that it is necessary, when the bead is parted by means of boiling sulfuric acid, to provide for the separation of palladium in the aqua regia extract of the residue and for the separation of platinum and rhodium from the sulfuric acid palladium solution.

Fulton and Sharwood (5) state that the sulfuric acid solution obtained from parting does not contain ruthenium or osmium. When ruthenium and osmium were present in the bead in appreciable proportions and the sulfuric acid solution was boiled, osmium was collected in sodium hydroxide solution and precipitated as the hydrated dioxide. When sodium bromate was then added to the sulfuric acid solution, ruthenium was distilled off and collected in sodium hydroxide solution and also precipitated as the hydrated dioxide. When the aqua regia extract was distilled, osmium was collected and precipitated as the dioxide. Fusion of the final residue with sodium peroxide and subsequent distillation of the fusion showed the presence of large quantities of both osmium and ruthenium.

Separation of Palladium from Large Amounts of Silver

Heretofore silver has usually been separated from palladium (and small amounts of other platinum metals) in the sulfuric acid solution resulting from the parting of the assay bead, by precipitating it as the chloride. The precipitate always occludes palladium. To overcome this difficulty silver is precipitated from a dilute solution, and the chloride is dissolved and reprecipitated. After concentrating the filtrates, a small amount of silver chloride may appear and have to be removed. Complete separation of the two metals by this method is tedious and time-consuming.

The precipitation of palladium dioxide at pH 6, used by Gilchrist (7) to separate palladium (together with rhodium and iridium) from platinum, can also be used to separate palladium from silver, and offers a direct method of removing palladium from the sulfuric acid solution, in the presence of relatively large amounts of silver. This was demonstrated as follows:

A palladium sulfate solution was prepared from palladium chloride by repeated precipitation of the dioxide according to the directions given by Gilchrist (7) and solution of the dioxide in sulfuric acid (1 to 1). To four 10-cc. portions of this acid solution 800-mg. portions of silver carbonate were added, followed by boiling to dissolve the silver sulfate. The resulting solutions were neutralized to pH 4 with sodium bicarbonate, using bromophenol blue as indicator. Each solution was then treated with 5 cc. of a 10 per cent solution of sodium bromate, boiled, and neutralized to pH 6, as indicated by bromocresol purple. After boiling the solution for 20 minutes, the precipitate of brown palladium dioxide was collected in a porcelain micro-Gooch crucible with asbestos mat (a small filter paper could be used) and washed with hot water of pH 6. The crucible was placed in a beaker and treated with 4 cc. of hot hydrochloric acid (1 to 1), in which the precipitate dissolved rapidly. The acid solution was diluted to about 30 cc., and filtered from the asbestos and a small amount of silver chloride. Palladium was precipitated from these solutions with dimethylglyoxime, ignited in air, reduced in hydrogen, cooled in carbon dioxide, and weighed. The results obtained were 0.0219, 0.0219, 0.0219, and 0.0218 gram. Direct determination of palladium in 10 cc. of the palladium sulfate solution yielded 0.0219 gram.

In applying this procedure to the sulfuric acid obtained in parting the assay bead, after diluting it and filtering off the

insoluble residue, the filtrate is evaporated to a volume of about 3 cc. The viscous residue is cooled only slightly, diluted with hot water, and the solution boiled if necessary to dissolve the silver sulfate. The separation of palladium is done as already described. Small amounts of rhodium, ruthenium, and platinum are likely to accompany palladium in the sulfuric acid parting. Rhodium and ruthenium will precipitate with palladium as dioxides but will not accompany it when it is finally precipitated with dimethylglyoxime. Traces of platinum which are carried down with the palladium dioxide, unless proper precautions are observed, will later contaminate the precipitate of palladium dimethylglyoxime if filtration of this precipitate is delayed longer than an hour.

The tendency of platinum to form a precipitate with dimethylglyoxime on standing was confirmed by adding an excess of the reagent to a solution of chloroplatinic acid prepared by dissolving platinum in aqua regia and eliminating the nitric acid. A blue precipitate, which has been described by Cooper (2), appeared within about 30 minutes. On the other hand, 0.1 per cent solutions of rhodium, iridium, ruthenium, and osmium, whether as sulfates or chlorides, failed to show any precipitate with dimethylglyoxime in 4 days. The observation that rhodium and iridium do not contaminate the palladium dimethylglyoxime precipitate has also been reported by Gilchrist (7).

Determination of Palladium and Platinum in Residue

The residue from the parting of the bead with sulfuric acid is digested with dilute aqua regia (1 to 5) to dissolve gold (if present), platinum, and residual palladium. If gold is absent, the solution is diluted with about 30 cc. of water for each 25 mg. of palladium, and the palladium separated from platinum by the dioxide precipitation, after which it is precipitated with dimethylglyoxime and added to the palladium obtained from the parting solution. Traces of rhodium and iridium which are dissolved by the dilute aqua regia will be precipitated with the palladium as dioxides, but will be eliminated by the precipitation with dimethylglyoxime. As previously noted, small amounts of platinum carried down by the dioxide precipitate may contaminate the dimethylglyoxime precipitate if filtration of the latter is delayed.

Reduction of platinum by means of sodium formate from a solution adjusted to pH 6 is recommended for the determination of platinum after the removal of palladium. Sodium bromate interferes with the reduction and must first be destroyed by evaporation with hydrochloric acid.

If gold is present, the hydrochloric acid solution of gold, platinum, and palladium is placed in a cup fashioned from 20 grams of sheet lead and evaporated carefully, silver is added and the whole is cupelled. The bead is parted with nitric acid in the usual manner and gold remains as a residue.

Treatment of Rhodium and Iridium

If rhodium and iridium are present in the assay bead, they remain as an insoluble residue after parting with sulfuric acid and treatment with dilute aqua regia. According to Fulton and Sharwood (4), treatment with strong aqua regia dissolves the iridium, leaving a residue which is considered to be rhodium, but the authors' experience does not confirm this. The literature records no satisfactory method for getting into solution the residue obtained at this stage of the assay procedures. Ignition with sodium chloride in a current of chlorine is extremely inconvenient. Sulfuric acid is used by Gilchrist (6) to dissolve freshly precipitated rhodium, and by Zhemchuzhnyi (13) in sealed tubes to dissolve rhodium sponge, but it scarcely attacks rhodium which has been previously cupelled with silver. Fusion with sodium peroxide or a mixture of sodium

peroxide and hydroxide in a silver or nickel crucible has been employed by many workers, including Claus (1), Noyes and Bray (10), and Wichers, Gilchrist, and Swanger (12), to convert refractory platinum metals and their alloys into soluble forms but not, in general, for quantitative purposes. A procedure based on this method of attack has been developed which results in complete solution of as much as 50 mg. of combined rhodium and iridium left after cupeling and parting the silver bead, and treating the residue with dilute aqua regia.

The aqua regia solution is filtered from the residue, and the paper containing the latter is dried and ashed in a silver crucible. About 1.5 grams of sodium peroxide are added, the crucible is covered, and the contents are heated to dull redness for 5 minutes. After cooling, the crucible is covered with water in a 250-cc. beaker. After the resulting reaction, the crucible is transferred to a small casserole and washed with dilute nitric acid. This solution and additional nitric acid to make 10 cc. of concentrated acid are added to the alkaline solution. Iridium forms a blue alkaline solution which turns yellow when acidified. Rhodium settles out as a brown substance which has not yet been identified but is presumably an oxide. After boiling for 15 minutes to dissolve silver, the solution is filtered from the brown rhodium compound.

The paper and contents are digested with 10 cc. of concentrated sulfuric acid in a small Erlenmeyer flask. Small quantities of fuming nitric acid are added from time to time, between intervals of boiling, to destroy organic matter, and digestion with the boiling sulfuric acid is continued until the solution becomes clear and yellow. The solution is then diluted somewhat, added to the nitric acid solution, and the whole evaporated to a volume of 3 cc. If sulfuric acid is added directly to the nitric acid solution, without filtering off the rhodium compound, the latter collects in rings on the walls of the beaker as evaporation progresses and is not easily gotten into solution. Separate treatment of the brown rhodium material, and filter paper, can be completed in not more than 20 minutes. Rhodium or iridium not attacked by the sodium peroxide fusion would appear as an insoluble residue after solution of the brown rhodium compound and destruction of the filter paper in sulfuric and nitric acids. In many trials of this procedure no trace of unattacked rhodium or iridium has been found.

The small volume of sirupy liquid obtained on evaporation of the combined solutions is cooled slightly (not enough to solidify) and diluted with hot water. After boiling to dissolve all salts, the rhodium and iridium are separated from the relatively large amount of silver by precipitating their dioxides at pH 6, exactly as was done to separate palladium from silver, except that 10 cc. of the 10 per cent solution of sodium bromate are used instead of 5 cc. The precipitate is filtered off, washed, and dissolved in hydrochloric acid in the same way as the palladium dioxide precipitate, except that warming on the steam bath is necessary to dissolve it. After removing and washing the crucible, the solution is first evaporated to a small volume, then diluted and filtered. The residue of asbestos and a small amount of silver chloride is thoroughly washed with hot water.

If a paper filter (7 cm., Whatman No. 42) is used instead of asbestos to collect the dioxides, most of the precipitate is dissolved from the unfolded paper into a 150-cc. beaker with hot hydrochloric acid. The paper is destroyed with 3 cc. of concentrated sulfuric acid and small quantities of nitric acid in a 50-cc. Erlenmeyer flask. After diluting and again evaporating to eliminate nitric acid, this solution is combined with the main solution of the dioxides and the whole diluted to precipitate silver chloride, which is then removed by filtering. If the silver chloride is colored, the paper and contents are again treated with sulfuric and nitric acids; then a few drops of hydrochloric acid are added, and the resulting solution is diluted and filtered into the hydrochloric acid solution. This treatment is repeated once more, if necessary.

In a number of experiments designed to test quantitative recovery of rhodium and iridium which had been dissolved by the foregoing procedure, pure rhodium and iridium sponges were used instead of a mixed residue previously cupelled with silver. This was done because it has not yet been established whether the residue left after treatment with dilute aqua regia is free from other metals, or whether losses of rhodium or iridium occur during cupellation. Rhodium was determined, in the solutions resulting from the procedure, by precipitation with hydrogen sulfide and ignition to metal, in the

manner described by Gilchrist (6). Similarly, Gilchrist's procedure was used for the determination of iridium. In both cases smaller volumes were used.

The results obtained in four trials of the procedure on rhodium and four on iridium are given in Table II.

TABLE II. SOLUTION OF IRIIDIUM AND RHODIUM BY FUSION WITH SODIUM PEROXIDE IN A SILVER CRUCIBLE

Sample No.	Iridium		Rhodium	
	Used Mg.	Recovered Mg.	Used Mg.	Recovered Mg.
1	25.1	25.1
2	24.8	24.6
3	24.8	24.6
4	24.3	24.2
5	23.5	23.5
6	27.4	27.4
7	29.4	29.0
8	28.6	28.2

Low results, such as No. 7 and No. 8, indicate that the dioxides were not completely dissolved from the Gooch crucible. All the results given have been corrected for blanks amounting to 0.7 or 0.8 mg., which are caused mainly by impurities, such as iron and copper, in the silver crucible. The amount of the blank is reduced if a smaller amount of sodium peroxide is used. This is possible when treating the small amounts of iridium and rhodium usually encountered in the assay of platinum ores and concentrates.

In addition to its analytical use, the procedure for the solution of rhodium and iridium has proved an efficient and rapid method for the preparation of salts from the pure metal sponges.

The Silver Crucible

Some of the silver crucibles used were purchased from Johnson Matthey and Company. The amount of silver corrosion during the 5-minute fusion with 1.5 grams of sodium peroxide is about 500 mg. or more. This means that an ordinary crucible of spun silver lasts for about twelve fusions.

It was decided to prepare thick-walled silver crucibles; and these were made by means of pure silver placed in a nickel crucible which was heated in a furnace until the silver melted. The whole was cooled slowly and the molded silver cut down to the required size in a lathe. One such crucible prepared by the authors has already made fifty fusions and will last many more. The outside dimensions of a suitable crucible may be suggested as: height, 2 cm.; top diameter, 2.4 cm.; bottom diameter, 2.1 cm.; wall thickness, 0.4 cm. Crucibles made by fusing silver chloride and soda ash often contain appreciable chlorides.

Summary

When a bead with a silver-platinum ratio of 12 to 1 is parted with boiling sulfuric acid it is necessary to provide for the separation of palladium in the aqua regia extract.

Palladium can be removed completely from the sulfuric acid parting solution by means of the dioxide precipitation.

Osmium, ruthenium, rhodium, and platinum are partially dissolved from the bead by means of boiling sulfuric acid.

Platinum salts with dimethylglyoxime produce an indigo-blue or bronze compound. Osmium, ruthenium, iridium, and rhodium salts dissolved in dilute hydrochloric acid or dilute sulfuric acid do not produce a precipitate on standing in contact with alcoholic dimethylglyoxime solution for 4 days.

A suitable condition for the sodium formate reduction of platinum is from solutions the acidity of which has been adjusted to pH 6.

Rhodium and iridium can be dissolved by a short fusion with a small proportion of sodium peroxide in a silver crucible and removed from the resulting silver solution by hydrolytic precipitation.

Acknowledgment

The authors are indebted to the International Nickel Company of Canada, Ltd., for a generous gift of platinum metals.

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RECEIVED October 29, 1935.

A Thermionic Titrimeter without Batteries

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SINCE the vacuum tubes in a Wheatstone bridge circuit used by Hiltner (3) and others (1, 4-7) are capable of simultaneously acting as rectifiers of alternating current and as statically controlled variable resistors for the bridge, it appeared possible to power a thermionic voltmeter with ordinary alternating current. Trial not only showed it to be possible but also showed that the mere substitution of alternating for the usual direct current power enabled the device to measure alternating as well as direct current applied voltages.

Many vacuum-tube voltmeters have been described for chemical purposes since their introduction by Goode (2). This multiplicity of offerings is not indicative of a generally unsatisfactory performance of vacuum-tube voltmeters but rather is the result of advances in electrical engineering which enable succeeding authors to offer operational improvements of real value. More recently Hiltner (3) introduced a novel method of reducing the grid current to an exceedingly low value, negligible so far as titrations are concerned. His method required no manual adjustments, as contrasted to previous methods of regulating the grid current. He attained alternating current operation by the conventional method of rectifying the alternating current before applying it to the tubes. In the interim between presentation of the titrimeter described in this paper at the 88th meeting of the AMERICAN CHEMICAL SOCIETY in September, 1934, and the present time, during which it was thoroughly tested and developed, a circuit very similar to Hiltner's has been offered by Garman and Droz (1). They used alternating current power through the usual means of first rectifying and filtering it. Their chief contribution is introducing into chemical literature and chemical vacuum-tube apparatus the principles of mu-balance in combination with a Wheatstone bridge circuit. This rather elegant method of eliminating the effects of line voltage variations is probably effective, but considerable use of the more simple circuit to be described has shown that it is stable enough for purposes of titration. This paper presents a much simpler modification of the Hiltner voltmeter, adapting the circuit to alternating current power without a special rectifying tube and using American vacuum tubes.

Because of the inherent stability of the Wheatstone

bridge at and near balance, the use of self-biasing, and the use of a twin-type tube to obtain the advantage of identical vacuum and thermal fluctuations for both triode systems, together with a heater-type cathode, the usual fluctuations in the voltage of commercial lines have so little influence on the device as to be entirely negligible for potentiometric titrations but great enough to prevent better than about 0.1 pH precision in pH measurements.

As the name implies, the titrimeter is more useful and reliable for making titrations than for measuring equilibrium voltages, as in pH measurements with hydrogen and quinhydrone electrodes. The titrimeter passes sufficient current (0.1 to 0.5 microampere) so that it will not read the zero current voltage of such cells, but it can be employed to determine pH by using standard buffers to determine the small correction due to this small current. It cannot be used with the glass electrode.

This titrimeter is distinguished from all others based on the principle of the Wheatstone bridge by the fact that the tubes in the arms of the bridge not only serve as variable resistors but also simultaneously rectify the alternating current used to power the device and thus do away with all batteries and the necessity of a rectifying tube and filter system. The result of this dual function of the tubes is a remarkably simple circuit that requires fewer parts and is therefore simpler and more economical to construct, more fool-proof, and more convenient to use. It does not easily get out of order. One of these instruments has been in frequent use for more than a year without giving any trouble. These advantages make it particularly suitable for chemists, who are usually not familiar with thermionic circuits.

Much experimental work has influenced the selection of the following circuit constants and materials as the best compromise with regard to sensitivity, stability, ease of operation, low grid current, convenient assembly, and general availability of parts.

Circuit Materials

TUBE. RCA-53. RCA-6A6 is identical in characteristics except that it has a 6.3-volt heater; otherwise it can be substituted for RCA-53 without change.

METER. Weston microammeter, type 440, scale 0-150, 75 divisions, 3.5-ohm coil.

TRANSFORMER. Since the power requirements are

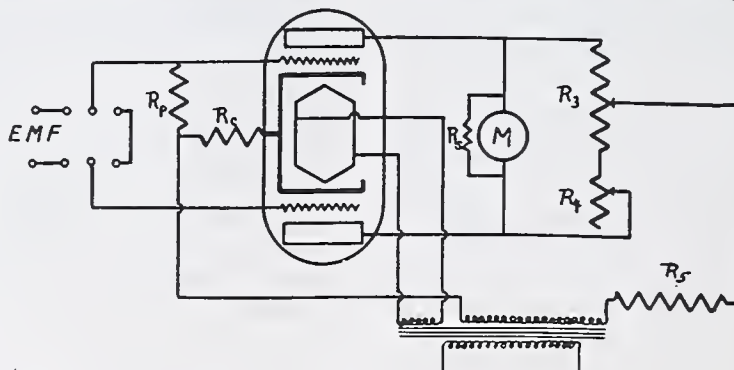


FIGURE 1. WIRING DIAGRAM

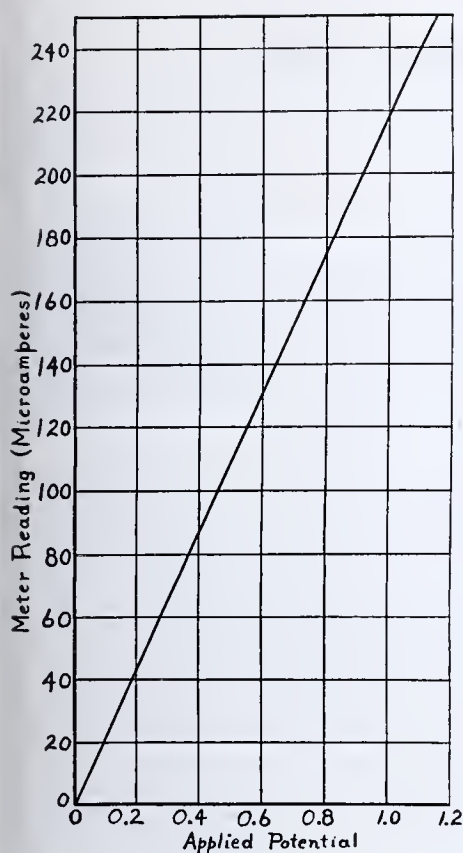


FIGURE 2. CALIBRATION CURVE

low, any good radio power transformer designed for midget sets and capable of delivering 10 m. a. at 220 volts for the heater will be satisfactory. Should the high-voltage secondary of the transformer to be used be higher than 220 volts, the excess is dissipated by R_5 (Figure 1).

GRID SWITCH. Any type of double-pole double-throw switch can be used. A Federal anti-capacity switch can be recommended for its neat appearance, ease of assembly, and ease of operation.

FIXED RESISTORS. R_p determines the grid current; its value depends on the characteristics of the tube, and since these vary it is impossible to give any definite value. Four tubes re-

quired values between 50,000 and 200,000 ohms. The determination of this value is the only adjustment the builder of the titrimeter is required to make. This resistor is very conveniently handled when designed to be inserted in grid leak mountings, thus facilitating adjustment whenever a new tube is put into operation.

R_c is a wire-wound resistor having 1000 ohms and capable of dissipating about 3 watts. Only a small fraction of this amount of power will actually be dissipated, but a wide margin is recommended as an aid in preventing a noticeable temperature rise which would change the resistance and cause drifts in the zero setting of the titrimeter.

R_5 is a wire-wound resistor whose value will depend on the value of the high-voltage winding of the transformer being used. It should be capable of dissipating three watts and have a resistance as given by the equation $R_5 = 480 (E_T - 220)$, where E_T = transformer voltage.

R_s is a shunt resistor for the microammeter and has the value of 20 ohms.

VARIABLE RESISTOR. R_1 is a midget-type radio potentiometer whose resistance is 2000 ohms. It must be wire-wound.

R_4 is a midget radio potentiometer whose resistance is 50 ohms. It must also be wire-wound. If a radio rheostat is chosen for R_4 it should be the type with no "off" position. The settings of R_3 and R_4 have no bearing on the accuracy or sensitivity of the titrimeter, but the value of R_4 for measuring sensitivity depends on the effective resistance of the tubes and of the meter, and the value given is the proper one for the parts recommended.

To minimize grid current the following procedure is used:

A fairly sensitive galvanometer (a pointer type is satisfactory) is connected to the e. m. f. binding posts and the grid switch is thrown to include the galvanometer in the grid circuit. R_p is then varied between wide limits when attached to first one grid and then the other. When R_p is attached to one of the grids the galvanometer will show minimum current for some certain value of R_p . This minimum current must under no condition exceed 0.5 microampere, and if the proper value of R_p is used the minimum can be made 0.1 microampere and even less. In a later paper it will be shown that a grid current no greater than this has no effect on the titration cell.

It is important that the positive voltage being applied in measurements be connected to the same grid to which R_p is connected. A reversal of applied polarity immediately causes a grid current of several tenths of a microampere to

flow through the grid circuit. It is of course necessary to adjust the connection of the microammeter so that the negative binding post is connected to the plate corresponding to the grid to which R_p is connected.

The voltage to be measured is connected to the e. m. f. terminals, but the bridge circuit must first be balanced by throwing the grid switch to connect the two grids directly, and adjusting R_3 and R_4 until the meter shows zero current. Upon throwing the grid switch to include the e. m. f. between the grids, the bridge will be unbalanced by this potential to the extent shown by the reading of the meter.

If a meter other than that specified is used, its resistance must not be greater than 50 ohms unless one is willing to sacrifice sensitivity. The sensitivity to be expected with the above materials is 0.22 microampere per millivolt impressed on the e. m. f. terminals. Various factors combine to make repeated readings of the same impressed voltage show a maximum variation of about 0.75 microampere, so that one cannot read with certainty closer than about 4 millivolts of applied potential.

Higher sensitivities than that given can be obtained by decreasing the value of R_c , the sensitivity being about double at zero ohms. However, there is a loss of stability as sensitivity is gained by this method and the difficulty of controlling the grid current is increased. Higher sensitivities may also be obtained with tubes of types 47, 2A5, and possibly 2A3, by using them in a two-tube circuit, but this is more than counterbalanced by the difficulty of maintaining calibration, by the necessity for using large resistors, by the greatly increased cost, and by other disadvantages.

As a direct-reading voltmeter it must be calibrated if the meter specified is used. Figure 2 shows a calibration curve. The calibration will not change until the tube emission becomes weak after very long use. The zero point should be checked before beginning a titration or making a voltage reading. The apparatus must be calibrated separately for measuring direct and alternating current voltages. The applied alternating current voltage to be measured must be phased properly. If the alternating current voltage being measured is of the same frequency as that applied to power the voltmeter and if it is also in phase or 180° out of phase with the voltage used for power, connecting the applied potential one way to the voltmeter causes no response, whereas the reverse connection results in meter readings proportional to the applied alternating current voltage.

Summary

A simple thermionic voltmeter without batteries has been described which operates from the alternating current lighting circuit, and is particularly convenient for potentiometric titrations. It is sensitive to 3 or 4 millivolts and the grid current, which is usually not over 0.1 microampere, has no effect on the titration cell.

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RECEIVED October 1, 1935. Presented before the Division of Physical and Inorganic Chemistry at the 88th Meeting of the American Chemical Society, Cleveland, Ohio, September 10 to 14, 1934. From a portion of a dissertation submitted by O. B. Hager, Jr., to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of doctor of philosophy.

A Continuous-Reading Electron-Tube Conductance Meter

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SEVERAL investigators have discussed continuous-reading conductance meters. Thus Jander and Schorstein (3) use a galvanometer with a bridge, while Sand and Griffin (1) use a dry rectifier with a bridge network. Treadwell (4) and Callan and Horrobin (2) supply the voltage to the cell and read relative resistance with a vacuum-tube device. Many of these methods are not very sensitive or lack general portability and require the use of calibration curves.

A vacuum-tube instrument has been constructed which incorporates an oscillator supplying audio frequency voltage to a self-contained bridge, a detector, and direct current meter which indicates the resistance of a conductance cell. These functions are performed with a single 6A6 tube whose circuit elements are properly arranged so that meter readings are a linear function of the resistance of the conductance cell. The instrument derives all power from alternating or direct current mains.

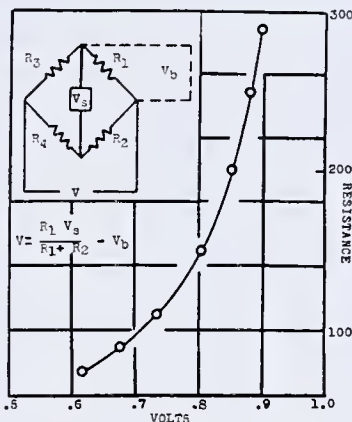


FIGURE 1. TYPICAL CURVE

Theory

The output voltage of a bridge is a parabolic function of the resistance of any one of its arms. A typical example is shown in Figure 1. The plate current-grid volts curve of a vacuum tube is not a linear function in the region of high negative values of grid voltage. A typical curve for a high μ triode is shown in Figure 2. (Direct current voltages were used in these calculations for simplicity and are permissible since the curves are used as illustrations only.) If these curves can be completely superimposed, an instrument may be constructed in which the plate current of an electron tube is a

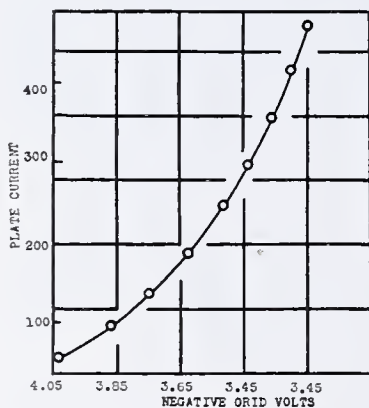


FIGURE 2. TYPICAL CURVE FOR HIGH μ TRIODE

C_4 . The voltage from the unbalanced bridge is applied to the primary of the step-up transformer T_2 . The stepped-up voltage is applied to the grid of the lower section of the triode which is negatively biased to zero plate current by adjustment of R_3 . A sensitivity control, R_2 , is used to attenuate the alter-

nating current voltage from the bridge while adjusting R_3 and to reduce the sensitivity, preventing the meter from reading off-scale in the performance of titrations where large changes in resistance are anticipated at the end point. Under these conditions of operation the meter will read the "off-balance" voltage of the bridge, the readings increasing as the bridge is progressively unbalanced.

As the resistance of the conductance cell increases, the shunt resistance between the plate side of choke L_1 and cathode also increases. This has the effect of increasing the voltage across the bridge terminals and distorts the grid volts-plate current curve shown in Figure 2. This distortion is desirable, since the resulting plate current will be more nearly a linear function of the resistance of the conductance cell.

The degree of linearity and sensitivity attained with this set-up is shown in Figure 4. Since the meter readings are linear with resistance over the range of plate current from 100 to 500 microamperes, the bridge must be unbalanced slightly before readings are taken. This setting may be performed after the titration has progressed to a certain extent, since the first readings are usually excluded in the final determination of the end point. This has a further advantage because almost full scale of the meter may be used in the region near the end point for greater accuracy.

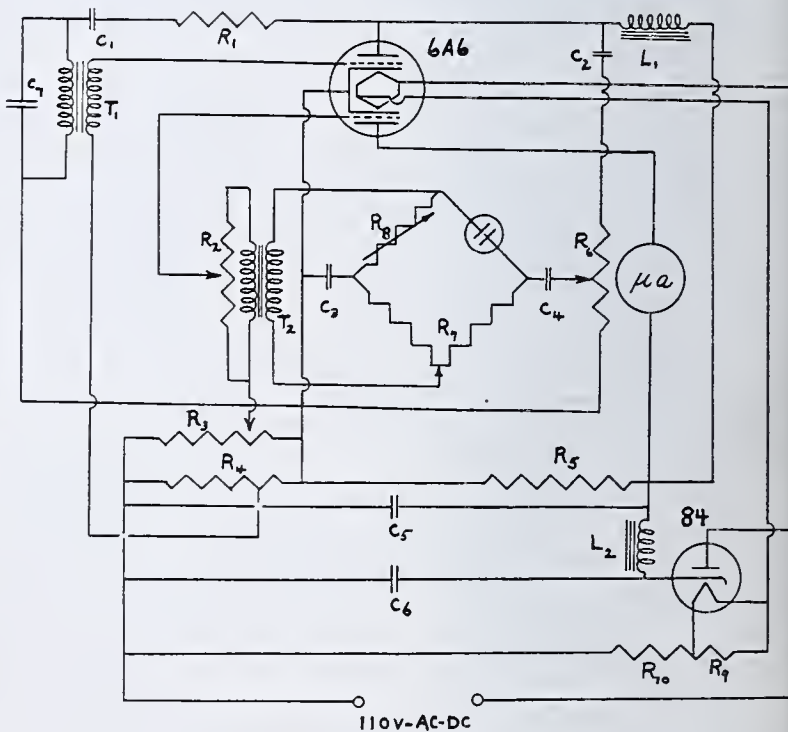


FIGURE 3. DIAGRAM

- R_1 . 5 to 7 megohms, 1 watt
- R_2 . 1-megohm volume control
- R_3 . 50,000-ohm volume control
- R_4 . Voltage divider, 1000 ohms, 25 watts
- R_5 . Voltage divider, 20,000 ohms, 25 watts
- R_6 . Volume control, 15,000 ohms
- R_7 . General radio potentiometer, 1000 ohms
- R_8 . General radio potentiometer, 100 ohms
- R_9 . 15 ohms, 100 watts
- R_{10} . 140 ohms, 100 watts
- C_1 . Condenser, 0.01 mfd., mica
- C_2, C_3, C_4 . Condensers, paper, 0.5 mfd., 200 volts
- C_5 . Electrolytic condenser, 8 mfd.
- C_6 . Electrolytic condenser, 4 mfd.
- T_1 . Low ratio audio transformer
- T_2 . Single-button carbon microphone transformer
- L_1 . Choke, 30 H.
- L_2 . Choke, 30 H. 200 ohms
- μa . 0-500 microammeter

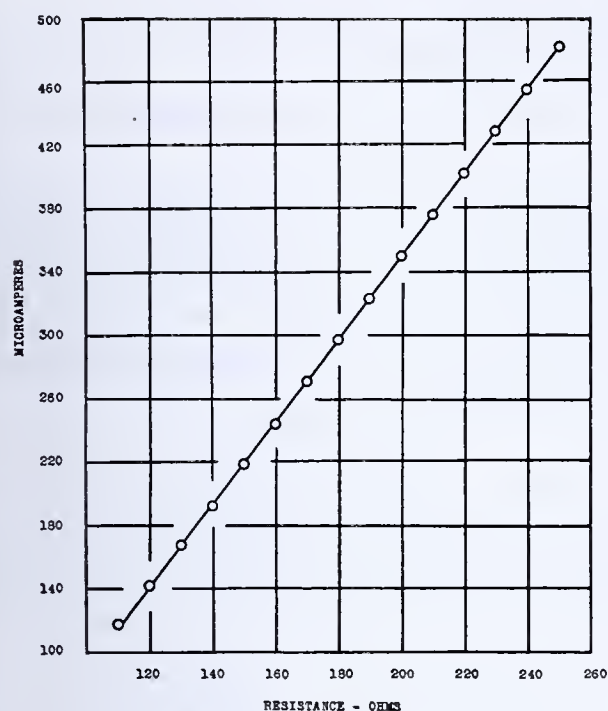


FIGURE 4. LINEARITY AND SENSITIVITY ATTAINED
Plate current—resistance of conductance cell

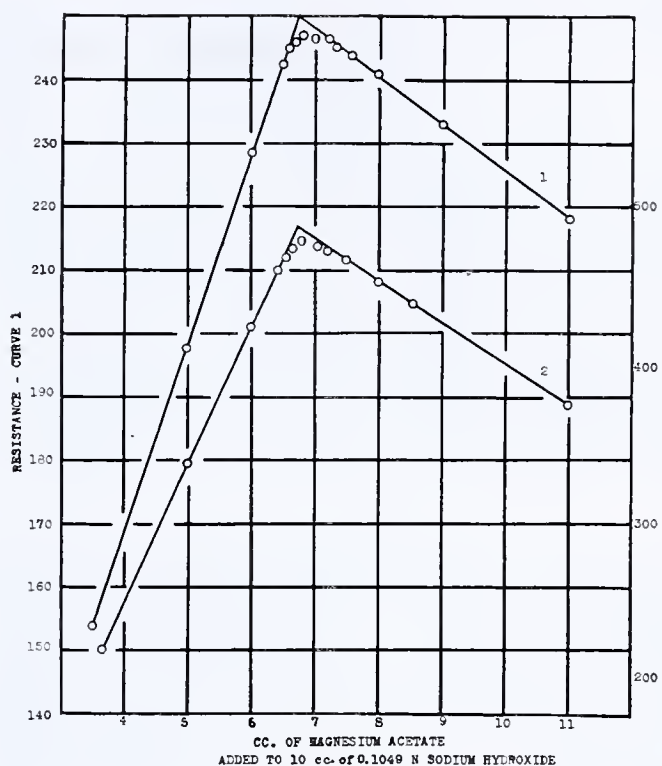


FIGURE 5. CONDUCTANCE TITRATION

Construction

The oscillating circuit was designed to offer a maximum in stability and yet lend itself to easy construction.

Transformer T_1 must be correctly poled to permit oscillations, and resistance R_1 should be as high as possible yet allowing sufficient energy feed-back to sustain oscillations. A high value of this resistance assures smooth operation and good wave form. The setting of R_1 is not critical and may be adjusted for maximum oscillator output (-2 to -3 volts are usually satisfactory). T_1 may be any low-ratio audio transformer, and since many of these units have a natural period of oscillation at approximately 1000 cycles per second, condenser C_1 may be omitted.

The bridge may be standard equipment or may consist of large-size wire-wound potentiometers since no calibration is required. Since the ratio of resistance in the bridge arms determines the curvature of the curve shown in Figure 1, the values must be as stated to attain the desired linearity. If, however, the apparatus is to be designed to measure higher resistance values of the conductance cell, the resistance of the bridge arms as well as the impedance of transformer T_2 should be increased proportionately. Meter readings are relative and the proper setting of resistors R_7 and R_8 may conveniently be determined for a particular range of resistance by substitution of a variable resistance box for the conductance cell. The settings of R_7 and R_8 are varied until equal increments of resistance produce equal increments of microamperes.

The inclusion of a rectifier and filter system permits satisfactory operation on both alternating and direct current mains.

Figure 5 illustrates a typical titration curve. In each case 10 cc. of 0.1049 N sodium hydroxide subsequently diluted to 200 cc. were titrated with magnesium acetate. The end point for curve 1, taken by the usual bridge methods, is 6.73 cc.; for curve 2 taken with the instrument it is 6.71 cc.

The error may be assumed to rest entirely with the inaccuracies encountered in the extrapolation.

The circuit described here does not represent the only one suitable for the purposes outlined. It represents rather a simple scheme which may be translated into a compact instrument and the cost of the parts, including the meter and cabinet, need not exceed twenty-five dollars. A more complicated circuit extending the principles described here could certainly be made in which the conditions of linearity are more closely approximated. It is the ardent hope of the author that such circuits will be devised to further the technique of conductance titrations.

Summary

A vacuum-tube conductance meter deriving power from alternating or direct current mains combining an audio oscillator-bridge and a detector-meter system has been described. The application to conductometric titrations has been illustrated and it has been shown that meter readings are linear with resistance over four-fifths of the meter range.

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When Is a Desiccator?

HAROLD SIMMONS BOOTH AND LUCILLE MCINTYRE, Western Reserve University, Cleveland, Ohio

WHEN the authors completed the study establishing porous barium oxide (*I*) as a drying agent comparable with phosphorus pentoxide, it became the practice in this laboratory to use barium oxide (furnished through the kindness of M. J. Rentschler of the J. H. R. Products Co., Willoughby, Ohio) as a reagent in desiccators, on account of its cheapness and its efficacy. It occurred to them that it would be interesting to learn the rate of drying a space, such as a desiccator, with barium oxide and the other common drying agents.

Apparatus

The method consisted of bringing air saturated with moisture into contact with the drying agent under the conditions which exist in a desiccator, and of observing the rate of decrease in the amount of moisture present in that air, as indicated by the decrease in pressure observed. It was decided that a manometer, on which the pressure could be read directly owing to a Torricellian vacuum on one side, could be used to measure the drop in vapor pressure sufficiently accurately for this purpose.

In preparation for a run, moist air was drawn through the gas-washing bottles through stopcocks 4 and 5, while 3 (Figure 1) was closed, into the gas holder, *D*, by applying suction to the outlet at the bottom of *D*. Water was then run into *D* from vessel *C* through stopcock 6 until the pressure inside *D* equaled that of the outside atmosphere. All stopcocks were closed and the moist air was allowed to stand overnight in *D*.

One hundred grams of the fresh drying agent were put into a Petri dish which just fitted the bottom of the desiccator. The lid on the desiccator was greased with a stopcock grease of proved low vapor pressure, and the cross piece of the wooden frame holding the desiccator in place was fastened down. A rubber stopper of a size near that of the handle of the desiccator lid was fastened to the wooden cross piece so that when the latter was in place, the pressure upon the handle of the cover of the desiccator was relieved by the elasticity of the stopper. The desiccator was sealed to the apparatus near stopcock 1 by DeKhotinsky cement.

Stopcock 2 was opened, and the manometer, *B*, and the desiccator were evacuated. Stopcock 2 was then closed and the apparatus allowed to stand overnight to be sure that no slow leaks would develop. The next day stopcocks 3 and 5 were opened and the water-saturated air was forced into the desiccator by allowing water to run into bottle *D* from vessel *C* through stopcock 6 until the pressure in the desiccator was about 760 mm. As soon as the stream of air was shut off, the vapor pressure was read on the manometer and the time recorded. The pressure was read at intervals of 1 minute until the fall in pressure was slow

and thereafter was read at intervals of 0.5-mm. change on the manometer. This was the approximate decrease during the 1-minute intervals first recorded. Readings were taken until the pressure change was so slow that it would not affect the curve materially. The apparatus was allowed to stand until the next morning, when the final reading was taken. At least six runs were made with each drying agent, but only the representative ones were plotted. This method, while rough, yielded some interesting information.

Results

Figure 2 shows representative curves for each drying agent used, the fall in vapor pressure being plotted against the time elapsed. While the results show little significant differentiation between the rates at which the air in a desiccator is dried by different desiccants, the uselessness of a desiccator as commonly used is clearly revealed when the curves are exam-

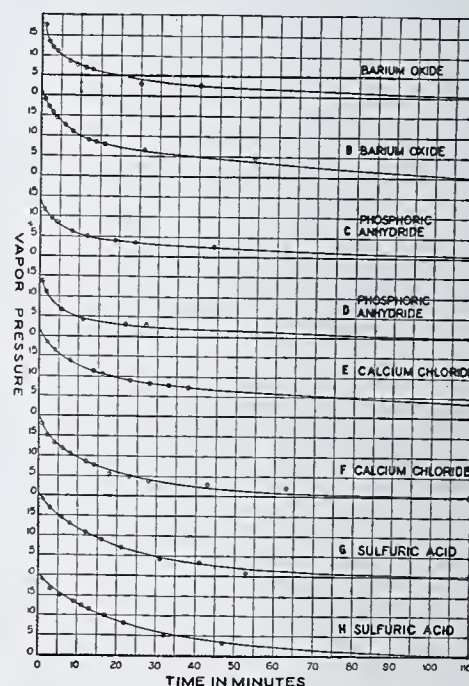


FIGURE 2. REPRESENTATIVE DRYING CURVES

ined. The average analyst has a holy respect for the power of a desiccator to keep his ignited crucibles dry during the cooling process, yet is careless about keeping the desiccator closed and about opening for only the briefest time. The writers have seen a student open a desiccator, go to the oven or electric crucible furnace, get his crucible, return, and put it in the desiccator to "cool in a nice dry atmosphere." Let us assume that half of the air in the desiccator has been displaced, and that the air let in is half saturated, or roughly that a partial pressure of 5 mm. of water vapor is now in the desiccator. The crucible will attain practically room temperature in 10 minutes, in which time the drying agent will have lowered the partial pressure of the water vapor in the air in the desiccator only 2 mm., while the crucible is simultaneously adsorbing the moisture from the air in the desiccator. Generally the air in the analytical laboratory is nearly saturated with moisture, so that the probable moisture content in the desiccator would be much higher.

Even some textbooks advise the student not to place the cover on the desiccator until the crucible has cooled somewhat or else the expansion of air will blow the cover off and break it! Why use a desiccator at all if that is the criterion? How can students following such advice ever get constant weight on a

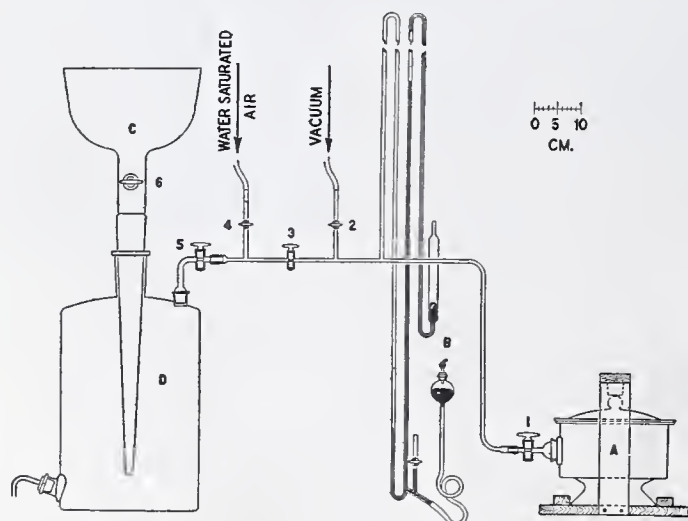


FIGURE 1. APPARATUS

gravimetric calcium determination? The authors tell students to hold the cover on and let some of the heated air escape if it will. The rather facetious title of this paper is inspired by these observations, in the hope that it will serve to arouse analysts to this unsuspected source of error.

However, in view of the moisture always inadvertently admitted, no matter how rapidly the desiccator is opened and closed, it is useless to use a desiccant of the highest absolute drying power such as phosphorus pentoxide, since the object cooling in the desiccator will ordinarily be removed for weighing before the space can be dried completely. Save for the danger of spilling, sulfuric acid should be satisfactory. If a neutral desiccant is desired, calcium chloride free from calcium hydroxide is useful. Where an alkaline drying agent is permissible, porous barium oxide is excellent, and is particu-

larly valuable in determinations affected by carbon dioxide, such as gravimetric calcium. Since barium oxide swells considerably on absorbing moisture, the bottom of the desiccator should not be more than half full.

Porous barium oxide is an industrial product, being produced in the first step in manufacturing barium peroxide, and is available more cheaply than anhydrous calcium chloride, which is difficult to prepare. The exhausted barium oxide can be used for the preparation of standard barium hydroxide solutions for alkalimetry.

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RECEIVED April 1, 1935.

A Versatile Low-Temperature Thermostat

G. B. HEISIG, University of Minnesota, Minneapolis, Minn.

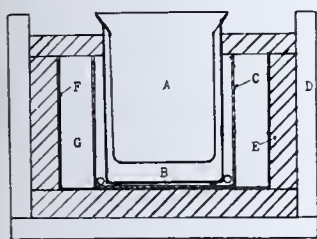


FIGURE 1

THE commercial production of solid carbon dioxide has made available an economical and convenient method of obtaining temperatures down to -78°C . A constant low temperature is desirable for many operations, such as the study of reaction rates, the saturation of a gas with a

definite quantity of a vapor, and the determination of vapor pressure, temperature, composition diagrams, etc.

A number of investigators have described thermostats which may be operated at low temperatures (1, 2, 4-6). Some are rather elaborate pieces of apparatus, while others are relatively simple. The thermostat described here is easily made from materials found in any well-equipped laboratory, and has been used to maintain a constant temperature in the range $+25^{\circ}$ to -75°C . The fluid used in the bath may be acetone, alcohol, or kerosene, depending on the temperature to be maintained. Acetone freezes at -94.6° and retains its mobility at the temperature of solid carbon dioxide. Alcohol becomes viscous below -40° . Kerosene may be used for temperatures to about -40°C .

The container for the bath is a 3-liter Pyrex beaker, A, which is set in a 4-liter beaker, B. The air space between the two beakers serves to prevent the bath from cooling too rapidly. The formation of ice between the beakers may be prevented by sealing the crack with rubber cement used to fill cuts in the tread of automobile tires. The nested beakers are placed in a can, C, whose diameter is 5 cm. (2 inches) greater than that of the larger beaker, and centered by a ring made from rubber tubing of appropriate size. The can containing the beakers is placed in a wooden box, D, fitted with cork lining, E, built around the square tin can, F. If a constant temperature is wanted for several hours only, the space between the outer beaker and can C is filled with a slush of well-crushed dry ice and alcohol. If a constant temperature is wanted for a considerable time, the space, G, is also filled with crushed dry ice.

The bath is stirred with a turbine paddle attached to a Bakelite or metal rod, the other end of which is connected to the shaft of a small induction motor. An induction motor is desirable to avoid igniting the vapors from the bath.

Since the bath is constantly being cooled, it is necessary to supply heat to maintain a constant temperature. This is done by means of a heating coil made from 10 cm. of No. 24 resistance wire welded or clamped to leads made of No. 18 iron wire, which are connected to the secondary terminals of a 25-watt toy transformer. The current in the primary circuit of the transformer is made and broken by a relay as the temperature varies. The proper amount of heat necessary to offset the cooling is obtained by adjusting the voltage.

The thermostatic element shown in Figure 2 is a bimetallic strip, A, made of brass and invar and consisting of four bows with the open end of the bows directed toward the long axis. The distance between the open ends of the bow will increase or decrease on warming, depending on whether the invar is on the inside or outside of the bow. A brass or preferably glass or Bakelite rod, B, rests on the lower end of the last bow. The upper end of the rod fits into a cup attached to a screw, E, threaded onto a piece of spring brass, C, one end of which has a fixed position. Screw E is adjusted so as to place a slight tension on the spring arm, C. The other end rises and falls with a change of temperature in the bath, making and breaking the grid current of a radio relay circuit (3). A thermionic relay control of some sort is required, since no sparking should occur between the contacts.

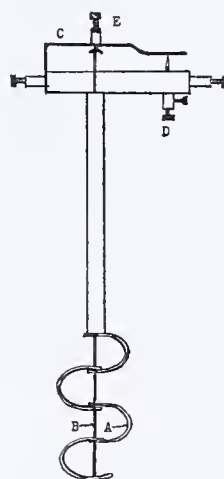


FIGURE 2

To start the thermostat, the bath is cooled to a temperature slightly below that wanted by pieces of dry ice in a small wire sieve, such as that used for straining tea or coffee, or a cup made of wire screen, immersed so that the liquid comes in contact with the cooling agent. The gas bubbles have only a short distance to go before reaching the surface of the liquid and the usual overflow is thus avoided. The stirring motor is started and screws E and D are adjusted so that heat is being supplied to the bath. When the proper temperature is reached the screws are adjusted so that the heat is discontinued.

To increase the temperature of the thermostat, it is only necessary to cause the heater to go on, and when the proper temperature is reached to adjust screw E, place a slight tension on rod B, and turn screw D so that the heater goes off.

The temperature of the bath is constant $\pm 0.01^{\circ}\text{C}$. About 5.5 kg. (12 pounds) of dry ice were required to maintain a temperature of -38.1°C . for nearly 18 hours and 45 kg. (100 pounds) were used during a week.

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Improved Apparatus for Isolation of Fluorine

Willard and Winter Method

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IN THE determination of small amounts of fluorine according to the method of Willard and Winter (2), hydrofluosilicic acid is distilled from a sulfuric or perchloric acid solution of the sample, the temperature of the solution being held at about 135° C. by the addition of water at the proper rate to maintain this temperature.

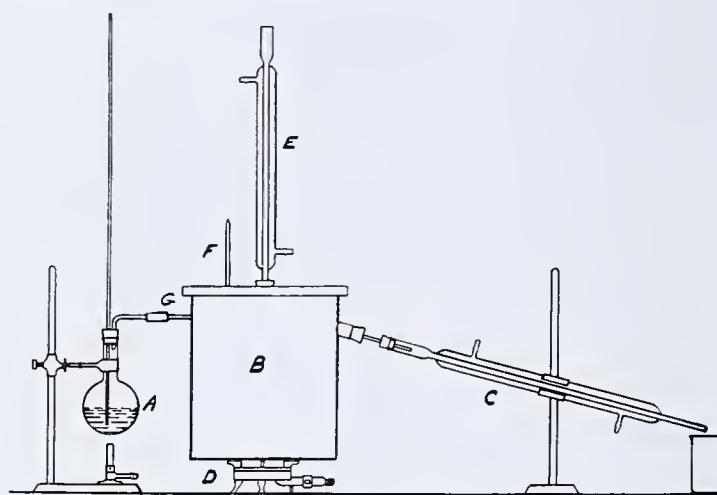


FIGURE 1. DIAGRAM OF APPARATUS

This method of distillation requires the undivided attention of the analyst if the temperature is to be maintained approximately constant. Moreover the addition of water, as liquid, to the hot contents of the flask results in considerable bumping with the attendant danger of contamination of the distillate. This is a source of error when determining fluorine in phosphates (1), as the phosphate carried over will react like fluorine in the subsequent titration and will thus lead to high results. Where such entrainment is suspected, it is customary to subject the distillate to another distillation under the same conditions. The phosphate carried over during the second distillation ordinarily will be negligible.

By the use of the apparatus herein described, superheated steam is substituted for water, thereby eliminating the danger of bumping; also the contents of the distilling flask are maintained at a constant temperature by being immersed in the vapors of a boiling liquid. The above-mentioned difficulties are thus avoided.

Apparatus

Referring to Figure 1, steam is generated in flask A which is provided with a safety tube, the purpose of which is to prevent the contents of the distilling flask from being sucked back in case the pressure in A falls below atmospheric. The steam passes from A into a copper tube which is wound around the inside of vessel B. (B was made of brass, but copper or steel would undoubtedly have been equally satisfactory.) This vessel, containing boiling tetrachloroethane, is heated by gas burner D and is provided with condenser E and thermometer F. In passing through the copper tube, the steam becomes superheated to the temperature maintained within the vessel. This superheated steam is then passed through a glass tube into the bottom of the distilling flask where it bubbles through the acidified sample and is subsequently condensed in C.

Figure 2 shows a detailed section of B and its contents. The heavy, removable lid has a machined groove in which a cork gasket is inserted. Since the organic vapor contained in B at-

tacks rubber, all stoppers are of cork and must be selected and drilled carefully if leaks are to be avoided. (Corks could be eliminated by using ground-glass joints. The cork through which the steam enters the flask can be eliminated by using a glass seal at this point. The obvious disadvantage is the increased danger of breaking the joint when assembling the apparatus for a determination.) In this laboratory the distilling flask used is of the Claissen type, but probably a simple distilling flask would be satisfactory. The tetrachloroethane used in B is the Eastman technical grade. It is noninflammable and boils at 145° C. A depth of about 2 cm. in the bottom of the vessel is sufficient.

According to Willard and Winter, there is danger of violent oxidation of organic matter by perchloric acid at temperatures exceeding 135° C.; they recommend the use of sulfuric rather than perchloric acid if the sample contains much organic matter. This substitution should be observed when tetrachloroethane is used as a heating liquid.

Procedure

The procedure in making a distillation is as follows:

Flask A is disconnected from the copper tube at the rubber connection, G (Figure 1). The distilling flask, which contains a few glass beads, the sample, and the perchloric or sulfuric acid, is placed in position, all joints (except G) are made tight, and the burner, D, is lighted. Since the sample is usually added as an aqueous solution or suspension, the dilution of the acid is ordinarily so great that the contents of the flask will begin boiling at a relatively low temperature, but the boiling point will gradually rise as the water distills off. When the rate of flow from condenser C becomes small, flask A, which has been made ready and is now delivering steam, is connected to the copper tube and the steam distillation allowed to continue until a sufficient quantity of distillate is collected.

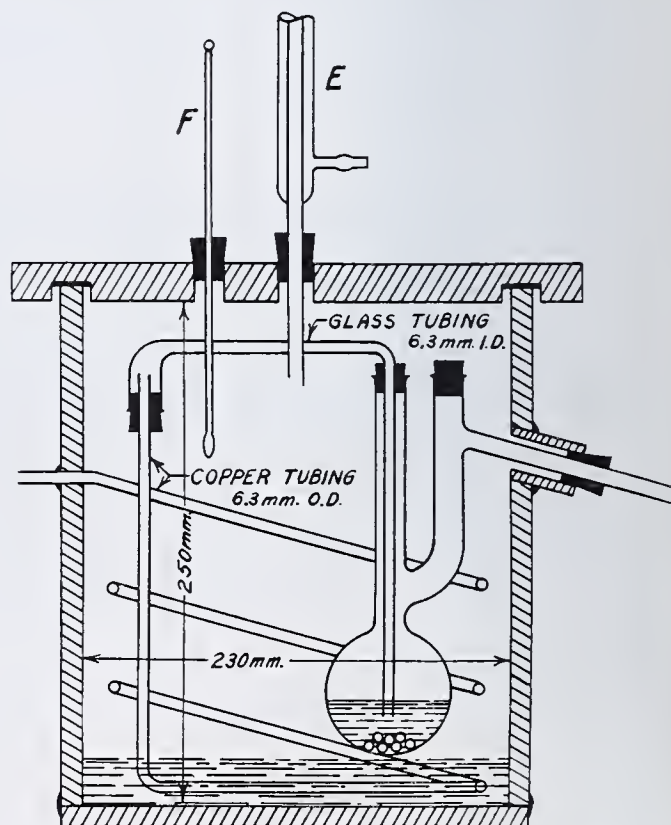


FIGURE 2. SECTION OF B AND ITS CONTENTS

A leaky cork will allow steam to pass into the organic vapor contained in vessel *B*. Even a small leak of this kind manifests itself as a noticeable drop in the temperature indicated by thermometer *F*.

Results

The apparatus has been in almost daily use in this laboratory for several months, and except for occasional leaks around corks has given no trouble whatever. Results ob-

tained with it, exercising only the precaution mentioned, have repeatedly checked those obtained with the original method of distillation using extreme care.

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Improved Micromanometer

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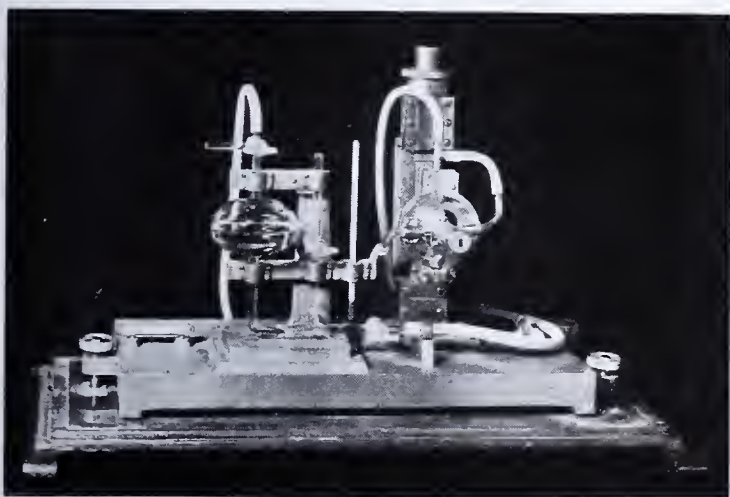


FIGURE 1

A SIMPLE, convenient, and rugged design of micromanometer, adaptable to routine measurements of minute pressures and pressure differentials, has been developed by engineers of the American Gas Association Testing Laboratories and successfully used by both the Cleveland and Los Angeles laboratories for several years.

The American Gas Association micromanometer consists, as shown in Figures 1 and 2, primarily of a heavy metal base, equipped with suitable leveling screws and indicating levels, and supporting reasonably massive columns carrying, respectively, the micromanometer screw assembly and the gage liquid reservoir. The reading meniscus lies in a short length of straight 0.25-inch glass tubing inclined at a slight angle from horizontal (generally in the neighborhood of 3°) and securely affixed to a thick-brass annular plate attached to the micrometer screw. This plate may be rotated and clamped to its carriage in order to permit adjustment of the slope of the meniscus tube. The other arm of the gage, comprised of a liquid reservoir bulb 3 to 4 inches in diameter, preferably with straight vertical sides, is clamped rigidly to the left brass column and connected to the movable meniscus tube by a length of thick-walled rubber tubing as short as possible and directed uniformly upward so that bubbles may not be trapped therein.

At its mid-point, the meniscus tube is supplied with a cross hair or engraved hairline. The meniscus is observed through a magnifying eyepiece of the variety commonly used for reading precise calibrated mercury thermometers. It is often necessary to locate a light disk, painted in flat white, behind the hairline and in line with the eyepiece, to facilitate reading in questionable light.

Forty threads per inch, corresponding to a linear pitch of 0.025 inch, should be cut on the micrometer screw, the diameter of which should not be less than 0.5 inch. At the Testing Laboratories the screw head is divided 25 divisions to the

circle, affording a division mark on the instrument for every 0.001 inch of pressure. By interpolating between the divisions in fifths, accurate readings may be made to 0.0002 inch.

Both openings of the glass gage system, the two pressure connections, are fitted with vent branches including glass stopcocks. All glass tubing clamps on the apparatus are fashioned of brass but lined with rubber to preclude breakage by shock or expansion.

The Testing Laboratories employ methyl alcohol as the gage liquid, since it does not affect the rubber tubing, possesses an accurately known specific gravity, and exhibits a low surface tension. Distilled water or any other liquid may, of course, be used with proper care so long as the specific gravity is known. If the instrument is constructed as indicated, precise readings may be made with it in 30 seconds. Additional speed of measurement may, of course, be attained if the slope of the meniscus tube is set at more than 3° from level, although some sensitivity is sacrificed thereby. A slope of less than 3° destroys the ease of adjustment necessary for routine usage and adds little or nothing to the accuracy of readings.

When using the micromanometer it is essential that the meniscus be brought to the point of adjustment on the cross hair always by turning the micrometer head in the same direction (that which draws the meniscus tube upward). This procedure overcomes errors due to play in the micrometer screw threads and failure of the movable assembly to drop against the friction of its ways.

Contrary to frequent belief, it is not mandatory that the sides of the liquid reservoir be absolutely vertical at the risk of error. So long as the volume of the liquid in the gage remains the same, the volume between the hair line (when the meniscus is adjusted upon it) and the surface of liquid in the reservoir must be the same, and therefore the level of the liquid in the reservoir bulb is, at the completion of any adjustment, identical with that obtained with atmospheric

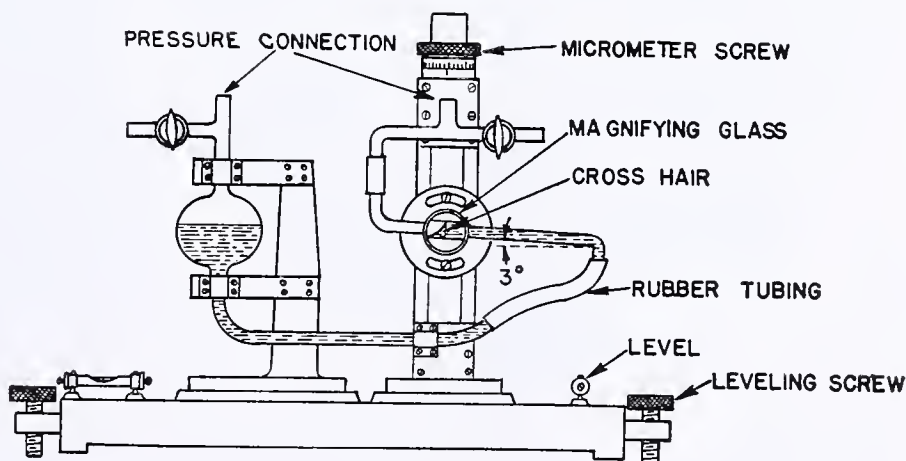


FIGURE 2

pressure at both points of pressure connection. The walls of the reservoir should be reasonably straight and its diameter reasonably large only to minimize the small errors due to evaporation, wetting of gage walls, and oscillation of the meniscus during adjustment.

In operation, the meniscus is simply adjusted to the hair-line with atmospheric pressure at both ends of the gage, a micrometer head reading taken, the pressure or pressure differential condition that is to be measured established by turning suitable cocks, the meniscus readjusted to the hair-line, and the micrometer head again read. The simple difference between the two readings, in marked divisions,

gives the pressure or the differential directly in 0.001 inch of gage fluid column. Since the instrument is so sensitive, it is often necessary to protect the pressure connections from drafts, to check on temperature variations, and to read the zero adjustment of the meniscus frequently whenever a long series of observations is being made.

Being at once elementary in theory, simple in operation, inexpensive in construction, rapid in adjustment, precise, direct-reading, and rugged, the American Gas Association Testing Laboratories' micromanometer should find wide use in many industrial fields.

RECEIVED January 7, 1936.

Device for Determining Rate of Siphoning in Metal Extraction Systems

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IN THE course of investigations on the solvent extraction of bituminous coal in a steel Soxhlet apparatus at elevated temperatures and pressures, an indicating system has been developed for determining the frequency of siphoning. Extraction in such an apparatus requires intermittent siphoning and, since this could not be observed, an indicator within the extractor was necessary. The indicating system is simple and inexpensive and could be adapted to any apparatus in which knowledge of frequency of transfer of liquid from one part to another was required, and in which visual observation was impossible or inadvisable. The apparatus developed has been in satisfactory operation for over 8 months,

using as solvents aniline and tetralin at temperatures to 400° C., and at pressures to 25 atmospheres.

As shown in Figure 1, the system consists essentially of a metal siphon tube, *A*, from the siphon cup above (not shown); a bucket arrangement, *B*; insulators, *C*; an insulated lead to the exterior, *D*; and an indicating system, *E*. All metal parts of the indicator proper except the main steel frame are made of nickel. The siphon tube, *A*, extends down into a grounded metal frame, *F*, which holds the buckets, *B*, loosely between two pivot bearings, *G*. A second metal framework, *H*, insulated from the first and held rigidly by small radio-type stand-off electrical insulators, *C*, serves as contact between the buckets and the wire lead to the exterior. This frame, *H*, also limits the downward motion of the buckets, which are counterbalanced by an attached weight, *K*. The insulated lead to the exterior, *D*, consists of a glass-insulated copper wire, *M*, to which is soldered a copper washer, *O*, compressed between two Bakelite washers, *N*, within the steel body of the closure as shown. The high-pressure closure is approximately 17.5 cm. (7 inches) above the extractor, but only at the higher temperatures is it necessary to cool the portion containing the Bakelite disks to prevent their decomposition.

Liquid overflowing through the siphon tube causes one of the buckets to fill, descend, and spill its contents. This movement of the bucket past the siphon tube, *A*, prevents more liquid from entering and raises the other bucket of the unit to a position where it now receives the overflow and in turn fills and descends. The downward motions of the buckets are stopped by the frame, *H*. The buckets continue this oscillation as long as liquid flows from the siphon tube. Each time contact of one of the buckets with *H* is made within the extractor, the electrical circuit through the dry cell, resistance, milliammeter, and steel wall of the extractor is completed and the pointer of the meter moves to its upper limit; when this contact is broken the pointer returns to zero position. By counting the swings of the pointer the frequency of siphoning can be determined, and knowing the approximate volume of each bucket, the amount of liquid being transferred can be estimated.

In the system used in this laboratory the external resistance in the indicating circuit, *E*, is so adjusted that current from one dry cell causes the meter to register one milliamperere when contact is made within the bomb. With this small amount of current flowing through the circuit, the deterioration of the nickel contacts used is negligible. In certain cases, it has proved desirable to use platinum contacts.

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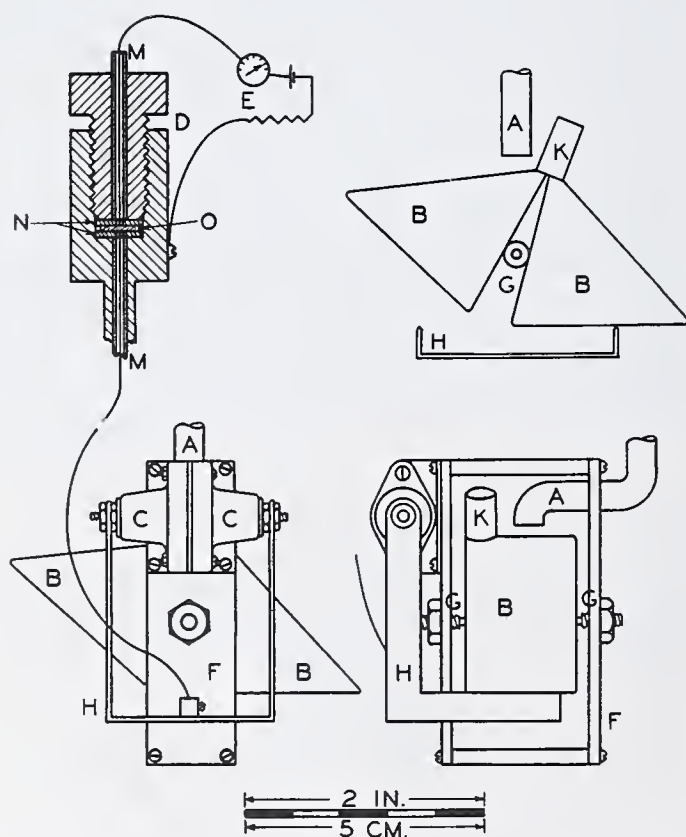


FIGURE 1. APPARATUS

Upper left, high-pressure closure
Upper right, essential parts

Lower left, front view
Lower right, side view

INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

Determination of Guanidines in Rubber Stocks and Consumption of Guanidines during Cure

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QUANTITATIVE determinations of various accelerators that may be present in vulcanized rubber stocks are necessary, not only for fundamental investigations into the mechanism of acceleration, but also for routine control analyses and the examination of unknown stocks. The determination of any organic material in vulcanized rubber stocks is beset with numerous difficulties, however, and reliable methods are scarce. For accelerators, the only ones described in the literature are the now generally employed copper oleate method for mercaptobenzothiazole and an extension of Callan and Stratford's (1) picric acid method for guanidines, both described by Wistinghausen (2). Using these two procedures, Wistinghausen made an extended investigation of the consumption of mercaptobenzothiazole and of diphenylguanidine (D. P. G.) during cure.

Considerable difficulty was encountered in this laboratory in the use of Wistinghausen's method. Especially with di-*o*-tolylguanidine (D. O. T. G.) stocks, the results were highly variable and the proportion of guanidine recovered seemed to be much smaller than that recovered by Wistinghausen from similar stocks. As a test of both the method and the technic, an uncured di-*o*-tolylguanidine tread stock was analyzed, since it was believed that, in this case, an effective procedure should account for substantially all of the guanidine put into the stock. The result was that little or no more guanidine was recovered from the uncured stock than from the same stock at an optimum cure. Guanidine recoveries from either one ranged from 30 to 50 per cent.

To find the reason why the guanidine could not be completely extracted from the uncured mixture, the procedure was applied to a series of stocks in which the ingredients of the original tread stock were omitted, one by one. Finally, it was found that when a simple mixture of acetone-extracted

When a guanidine accelerator is milled into acetone-extracted rubber, the guanidine cannot be completely recovered from the rubber by acetone extraction. If the mixture of rubber and guanidine is treated with a hydrolyzing agent, the bound guanidine is freed and 100 per cent recovery can be made. Bound guanidine is also present in cured stocks, for when these stocks are treated with benzene and dilute aqueous hydrochloric acid, or with wet acetone, higher guanidine recoveries are obtained than by extraction with dry acetone.

Based on the above findings, a new hydrolytic procedure for determining guanidines in cured stocks has been developed. Data on several stocks analyzed by this method and by the Wistinghausen (acetone extraction) method, and the resulting consumption-curing time curves are presented for comparison.

rubber and di-*o*-tolylguanidine was extracted with acetone, a part of the di-*o*-tolylguanidine, amounting to 0.2 to 0.4 per cent of the guanidine on the rubber, was unextractable. Apparently the di-*o*-tolylguanidine was bound by, or formed a compound with, the rubber and/or the non-extractable protein of crude rubber. It was already known, however, that if a mixture of rubber and guanidine is swollen in a rubber solvent and shaken with dilute acid, all the guanidine is transferred to the aqueous phase wherein it can be determined as the picrate or by back-titration with alkali. Accelerator master batches have been analyzed by such a procedure for some time.

Thus, it seemed probable that, if all the guanidine could be recovered from an uncured mix by such a method, whereas it could not be completely recovered by acetone extraction, a

higher recovery of guanidine might be obtained from cured stocks by treatment with an aqueous acid and a swelling agent than by acetone extraction. This proved to be the case. The cured di-*o*-tolylguanidine tread, from which only 30 to 50 per cent of the guanidine could be recovered by acetone extraction, yielded 75 per cent or more of the original amount of guanidine when a method involving treatment with benzene and dilute acid was used. The increased amount of guanidine was obtained by the latter method because of the hydrolyzing action of the aqueous acid rather than the swelling action of benzene. This was shown by extracting the cured tread with benzene and then shaking the benzene extract solution with dilute acid. The amount of guanidine recovered in this way was essentially equal to that obtained by extraction with dry acetone. Furthermore, extraction with wet acetone removed much more guanidine from the stock than extraction with dry acetone, although a 20-hour extraction with acetone containing 2 per cent of water did not effect as high a recovery

of guanidine as could be obtained with benzene and aqueous acid. It was also found that the guanidine recovery was highly variable if, when the Wistinghausen procedure was followed, the acetone extractions were run without particular attention to keeping the acetone absolutely dry.

A brief study of the apparent consumption of guanidine during cure was made, using both Wistinghausen's method and the new method, which yields a higher guanidine recovery from a cured stock and complete recovery from an uncured stock. A comparison of the accelerator consumption curves obtained by the two different methods is presented.

Four different stocks were investigated, A, B, C, and D. Stocks A and B are duplications of two stocks used by Wistinghausen. Stocks C and D are present-day tread compounds, the former containing diphenylguanidine, the latter di-*o*-tolylguanidine.

TABLE I. STOCKS INVESTIGATED

	Stock A	Stock B
	<i>Parts</i>	<i>Parts</i>
Rubber (crepe)	100	100
Sulfur	3.8	3.8
Thermatomic black	38.3	38.4
D. P. G.	1.44	1.38
Zinc oxide	3.8
	143.54	147.38
D. P. G. content, %	1.00	0.94
	Stock C	Stock D
	<i>Parts</i>	<i>Parts</i>
Rubber (smoked sheet)	100	100
Sulfur	2.8	2.8
Zinc oxide	6.6	6.6
Rubber channel black	46.2	46
Stearic acid	3.3	3.3
Pine tar	3.9	3.9
Antioxidant ^a	1.0	1.0
Accelerator	1.04 (D. P. G.)	0.82 (D. O. T. G.)
	164.84	164.42
D. P. G. content, %	0.63	
D. O. T. G. content		0.50

^a 92.5 per cent phenyl- α -naphthylamine, 7.5 per cent *m*-toluylene diamine.

Each stock was cured 10, 30, 60, and 90 minutes at 307° F. (152° C.). Stock C was also cured 30, 60, 90, and 120 minutes at 290° F. (143° C.). Much of the preliminary work was done on stock D, cured 90 minutes at 290° F. (143° C.). Most of the other cures were beyond the optimum, as far as desirable physical properties are concerned. For the stocks cured at 307° F. (152° C.) the optimum time is probably about 25 minutes, while for those cured at 290° F. (143° C.) the optimum time is about 90 minutes.

In preparation for analysis, the stock, where possible, was finely ground to "springs" on a cold mill. Uncured or under-cured stocks that could not be crumbled were sheeted as thinly as possible and cut into small pieces.

The procedure used for the analysis of the stocks by the acetone-extraction method varied slightly but not essentially from that described by Wistinghausen. This slight modification of the Wistinghausen method and the new method involving hydrolysis are described below.

Method of Analysis

WISTINGHAUSEN METHOD. A 20-gram sample of the stock is extracted with acetone for 16 hours in a Soxhlet extraction apparatus. The acetone is completely removed from the extract by evaporation and the residue is dissolved in 20 cc. of ether. Thirty cubic centimeters of approximately 0.1 *N* hydrochloric acid are added to the solution and the mixture is heated on the steam plate for 5 or 10 minutes longer than is required to evaporate the ether. The hot aqueous solution is then poured through a filter. This treatment with ether and hot dilute acid is repeated twice to transfer all the guanidine to the aqueous acid solution which is allowed to stand at least 12 hours and then again filtered cold. The volume is adjusted to approximately 100 cc. and an equal volume of saturated aqueous picric acid solution is added. This mixture is heated on the steam plate for 1 hour. Heating causes the precipitate that first forms to redissolve.

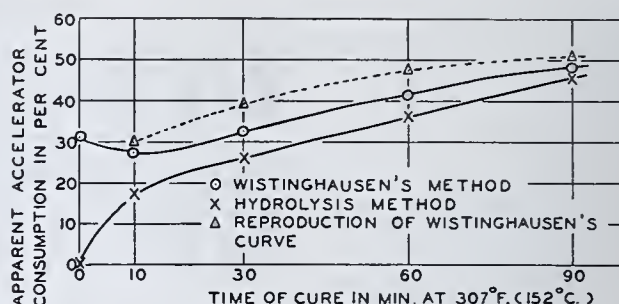


FIGURE 1. ACCELERATOR CONSUMPTION IN A
Wistinghausen's base stock

The heating period was found to be particularly necessary for di-*o*-tolylguanidine determinations, as di-*o*-tolylguanidine picrate forms slowly and incompletely in the cold. On cooling and standing, the diphenylguanidine picrate usually reprecipitates in crystalline form, but the di-*o*-tolylguanidine picrate only infrequently reprecipitates in this way. The precipitate should be allowed to stand for at least 12 hours before filtering. For di-*o*-tolylguanidine, especially, a longer period (48 hours) seems to help the character and quality of the precipitate. The filtration is carried out on a Gooch crucible lined with filter paper, the precipitate being completely transferred to the crucible with the aid of a "policeman" and a small amount of water. The precipitate is finally dried to constant weight in a 100° to 110° C. oven. An addition of 5 mg. is made to the weight of the picrate in the case of the di-*o*-tolylguanidine picrate and 8 mg. in the case of the diphenylguanidine picrate to correct for the slight solubility of these picrates in the 200-cc. mixture of saturated picric acid solution and 0.1 *N* acid. These solubility corrections were obtained from direct determinations of the solubility of the pure picrates in such a mixture at room temperature. For diphenylguanidine, the amount of guanidine is 48 per cent of the corrected weight of the picrate and for di-*o*-tolylguanidine, 51 per cent of the corrected weight of its picrate.

HYDROLYSIS METHOD. A 20.0-gram sample of the finely divided stock, 400 cc. of benzene, and 50 cc. of approximately 0.1 *N* hydrochloric acid are placed in a 1-liter flask so arranged that constant agitation of the mixture and refluxing of the benzene can be carried out together and the aqueous layer can be conveniently removed from the rest of the mixture, preferably without removing the whole mixture from the flask. A convenient apparatus for this purpose is a 1-liter Erlenmeyer flask to which has been sealed, near the base and projecting to the side, a stopcock outlet. By means of an ordinary addition tube placed in the neck with a cork stopper, the flask can be equipped with a stirrer and a reflux condenser. No mercury seal is necessary. The flask is heated, conveniently, by means of an electric hot plate.

Refluxing and brisk stirring of the mixture are continued for 1 hour. The condenser and stirrer are then removed, the flask is set on its side in a tripod, and the aqueous layer drawn off.

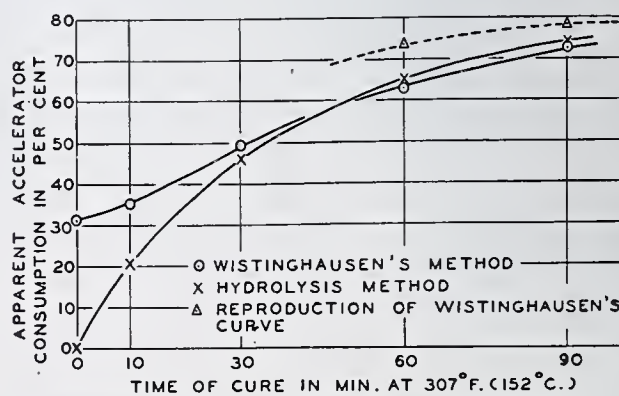


FIGURE 2. ACCELERATOR CONSUMPTION IN B
Wistinghausen's 3.8 per cent zinc oxide stock

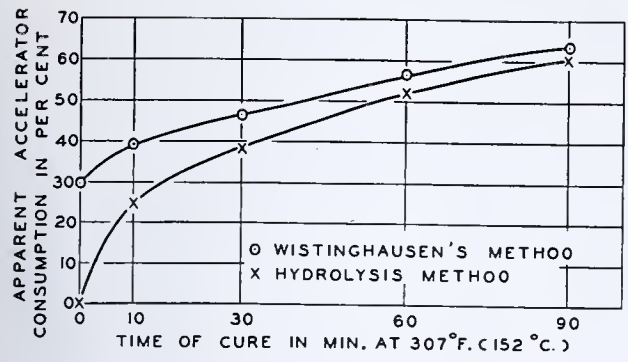


FIGURE 3. ACCELERATOR CONSUMPTION IN C
Diphenylguanidine tread stock, cured at 307° F. (152° C.)

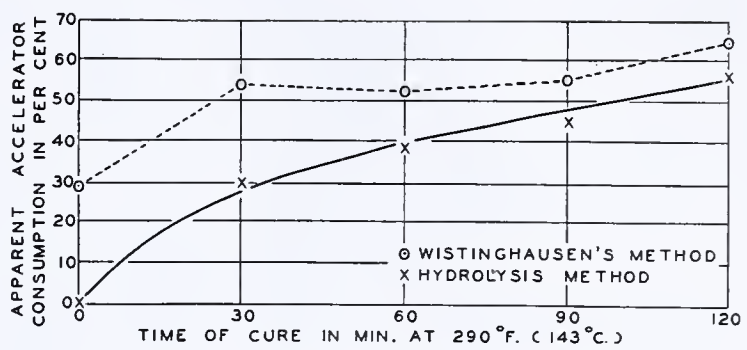


FIGURE 4. ACCELERATOR CONSUMPTION IN C
Diphenylguanidine tread stock, cured at 290° F. (143° C.)

At the temperature of refluxing benzene, little or no emulsification takes place. Another 50-cc. portion of dilute acid is added and the procedure is repeated. After a third similar treatment with acid, all the recoverable guanidine in the stock has been removed by the acid. The combined acid solution is allowed to cool completely and is then filtered. The filtered solution is clear and usually slightly yellow. The volume is adjusted by evaporation to about 100 cc. and an equal volume of saturated aqueous picric acid solution is added. The rest of the procedure is identical with that described above for the Wistinghausen method.

Besides the fact that it yields higher recoveries of guanidine through hydrolytic splitting of the bound guanidine complex, the hydrolysis method possesses several advantages as an analytical method over the Wistinghausen method. The quality of the picrates is much better, especially in di-*o*-tolylguanidine determinations. In the Wistinghausen method, picrates are frequently obtained which are noncrystalline, dark brown, and melt 20° C. lower than that of the pure picrate, whereas in the present method they are always crystalline, bright yellow, and seldom melt more than 6° C. lower than the pure picrate. Because the picrates obtained are purer and because the variability introduced by different moisture contents in the acetone extractions in the Wistinghausen procedure is not present, the results obtained by the hydrolysis method usually check much better than those obtained by the Wistinghausen method as used in this laboratory. For qualitative purposes only, the hydrolysis method is very rapid, a half hour's stirring and refluxing being sufficient to remove the greater portion of the guanidine. A qualitative determination requires only 2 or 3 hours' time from the beginning of the determination to obtaining the characterizing melting point of the picrate.

The modification of the above method to determine the guanidine in an uncured stock by precipitation as the picrate is as follows:

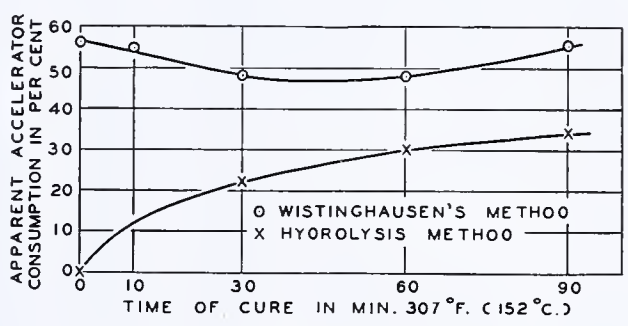


FIGURE 5. ACCELERATOR CONSUMPTION IN D
Di-*o*-tolylguanidine tread stock

A 10.0-gram sample is dissolved in 400 cc. of benzene by means of stirring and heating. If small bits of incompletely dispersed stock persist in the cement, no harm is done. Fifty cubic centimeters of approximately 0.1 *N* hydrochloric acid and 50 cc. of water are added and the mixture is stirred and heated for 20 to 30 minutes. The benzene is then evaporated while stirring is continued. When evaporation is complete, the rubber remains in a porous, spongy mass in the aqueous solution. The latter, containing most of the guanidine, is poured off. The remaining traces of guanidine can be removed from the stock by digesting for a few minutes with each of two more successive 50-cc. portions of 0.1 *N* acid. The procedure is then continued as described above.

Analytical Data

The analytical results given in Tables II and III are largely self-explanatory. Table II covers the preliminary work.

In the first three tabulated determinations (Nos. 29, 1, and 2), the uncompounded guanidines, dissolved in 100 cc. of 0.1 *N* hydrochloric acid, were precipitated with an equal volume of

TABLE II. PRELIMINARY RESULTS

Determination No.	Stock	Method	Wt. of Picrate		Av. Wt. of Picrate Corrected for Solubility	Accelerator Recovered	Apparent Accelerator Consumption	M. P. of Picrate ° C.	Remarks
			A Mg.	B Mg.		%	%		
29	D. P. G. (50 mg., commercial)	...	94.1	95.1	102.6	98.7	..	163-5 ^a	Theoretical wt. of picrate, 104.0 mg.
1	D. O. T. G. (50 mg., pure)	...	93.2	93.0	98.1	100.0	..	158-60	Theoretical wt. of picrate 98.0 mg.
2	D. O. T. G. (50 mg., commercial)	...	91.1	91.3	96.2	98.2	..	158-60	Three 1-hr. periods
3	D. ^{b,c}	H ^d	144.3	145.4	150.0	76	24	..	Three 2-hr. periods
5	D.	H	142.2	138.3	Three 8-hr. periods
7	D.	H	132.5	138.5	Commercial acetone
10	D.	W ^e	125.1	124.7	130	66	34	..	Dry c. p. acetone
11	D.	W	86.3	86.0	91	46	54	..	Commercial acetone + 10% water
12	D.	W	113.5	117.4	Commercial acetone + 2% water
14	D.	W	127.9	127.3	Benzene extraction
9	D.	...	80.0	78.8	84	43	57	..	

^a The m. p. of diphenylguanidine picrate is 170° C.; of di-*o*-tolylguanidine picrate, 162-3° C.
^b Cured 90 minutes at 290° F. (143° C.).

^c Theoretical amount of guanidine picrate for D, 196 mg.
^d Hydrolysis method.
^e Wistinghausen method.

TABLE III. ANALYTICAL DATA

Determination No.	Stock	Cure		Method	Wt. of Picrate		Av. Wt. of Picrate Corrected for Solubility	Accelerator Recovered	Apparent Accelerator Consumption	M. P. of Picrate ° C.
		Time Min.	Temp. ° F.		A Mg.	B Mg.		%	%	
65	A ^a	0	307	W	269.6	289.9	287	69	31	158-61 ^b
47	A	10	307	W	296.3	296.4	304	73	27	163-5
48	A	30	307	W	273.1	268.4	279	67	33	163-5
49	A	60	307	W	234.3	237.9	244	58	42	162-4
50	A	90	307	W	208.7	209.2	217	52	48	162-4
34	A	10	307	H	338.1	336.9	306	83	17	163-5
23	A	30	307	H	301.4	302.4	310	74	26	162-4
24	A	60	307	H	255.7	254.9	263	63	37	162-4
25	A	90	307	H	219.3	217.6	226	54	46	162-4
66	B ^c	0	...	W	265.0	256.9	269	69	31	160-2
43	B	10	307	W	255.5	239.2	255	65	35	161-4
45	B	30	307	W	193.0	188.8	199	51	49	157-60
44	B	60	307	W	135.4	136.9	144	37	63	151-5
46	B	90	307	W	94.7	96.2	103	27	73	154-7
26	B	10	307	H	299.1	296.0	306	79	21	162-5
27	B	30	307	H	204.9	203.3	212	54	46	162-5
28	B	60	307	H	131.1	128.3	138	35	65	162-4
31	B	90	307	H	90.0	93.7	100	26	74	160-3
64	C ^d	0	...	W	182.7	174.6	186	71	29	158-61
51	C	10	307	W	152.7	...	161	61	39	160-3
52	C	30	307	W	132.5	134.2	141	54	46	161-4
53	C	60	307	W	112.8	101.7	115	44	56	155-9
54	C	90	307	W	86.6	88.9	96	37	63	160-2
63	C ^f	0	...	H	123.0	119.0	129	99	1	164-6
39	C	10	307	H	185.7	188.6	195	75	25	162-4
40	C	30	307	H	157.9	152.4	163	62	38	161-3
38	C	60	307	H	117.7	119.9	127	48	52	161-3
37	C	90	307	H	96.2	96.3	104	40	60	160-3
64	C	0	...	W	182.7	174.6	186	71	29	158-61
60	C	30	290	W	111.4	113.3	120	46	54	158-62
61	C	60	290	W	112.1	122.7	125	48	52	157-61
62	C	90	290	W	118.0	103.2	118	45	55	157-61
59	C	120	290	W	94.4	86.3	98	37	63	157-61
63	C ^f	0	...	H	123.3	119.0	129	99	1	164-6
19	C	30	290	H	174.6	173.1	182	70	30	162-4
17	C	60	290	H	156.7	153.3	163	62	38	162-4
20	C	90	290	H	136.3	135.6	144	55	45	162-4
21	C	120	290	H	108.3	108.5	116	44	56	162-4
67	D ^e	0	...	W	76.8	82.5	85	43	57	141-6
57	D	10	307	W	81.5	83.9	88	45	55	141-6
58	D	30	307	W	96.8	...	102	52	48	141-6
55	D	60	307	W	103.6	90.0	102	52	48	141-5
56	D	90	307	W	76.9	90.5	89	45	55	141-5
36	D	30	307	H	146.9	...	152	78	22	158-60
41	D	60	307	H	131.6	134.1	138	70	30	158-60
42	D	90	307	H	122.1	125.5	129	66	34	158-60

^a Theoretical amount of guanidine picrate, 417 mg.

^b The m. p. of diphenylguanidine picrate is 170° C.; of di-*o*-tolylguanidine picrate, 162-3° C.

^c Theoretical amount of guanidine picrate, 390 mg.

^d Theoretical amount of guanidine picrate, 262 mg.

^e Theoretical amount of guanidine picrate, 196 mg.

^f 10.0 gram sample.

picric acid solution to check the completeness of the precipitation. When the 5- and 8-mg. corrections for solubility were added to the weights of the picrates obtained, the results were satisfactory. The next three determinations (Nos. 3, 5, and 7) were run to gain some idea as to the proper length of time for the extraction period in the hydrolysis method. It was concluded that there was no reason for continuing these extraction periods for longer than an hour. The next four determinations (Nos. 10, 11, 12, and 14) were made, employing various acetone extraction procedures as indicated under "Remarks," and show the variation in results caused by the introduction of water. The last determination (No. 9) was run by extracting the stock with dry benzene and then determining the guanidine in the filtered extract by hydrochloric acid extraction and precipitation in the usual manner.

Since the results obtained were substantially the same as those obtained with dry acetone, it is evident that the acetone-insoluble guanidine in the stock is liberated by the hydrolytic effect of the acid rather than by the swelling effect of the benzene.

Table III is a tabulation of the results obtained on the various cures of stocks A, B, C, and D. The curves shown in Figures 1 to 5, inclusive, were obtained by plotting the apparent accelerator consumption—i. e., the difference between the theoretical and the determined value—against the time of cure. Figures 1 and 2 also contain a reproduction of Wistinghausen's curves for stocks A and B, which are inserted for the sake of comparison. In Figure 4, no reasonable curve representing accelerator consumption as determined by the Wistinghausen method can be drawn through the plotted points.

It will be necessary to obtain further data, especially for

short curing periods, in order to determine the true course of the curve.

Discussion of Results

Reference to Figures 1, 2, and 3 shows that, for diphenylguanidine stocks, the curves obtained by the hydrolysis and Wistinghausen methods are approximately identical over the greater part of their range. From this it might be inferred that, for practical purposes, the guanidine could be determined by either method. This would be true if we were interested in overcured stocks, but it should be recalled that, for commercial stocks, only the first quarter of the curves (Figures 1, 2, or 3) would be involved. Figure 4 (diphenylguanidine stock cured at 290° F., 143° C.) shows the situation in the range of the optimum cure somewhat better, as far as distance between the curves is concerned, although the true course of the Wistinghausen curve is not known. In the case of di-*o*-tolylguanidine stocks (see Figure 5), the difference between the two curves is much more pronounced. There is apparently more extensive compound formation with di-*o*-tolylguanidine than with diphenylguanidine and this addition compound of di-*o*-tolylguanidine is less readily destroyed. This behavior may be the cause of the greater accelerating activity of di-*o*-tolylguanidine as compared to diphenylguanidine.

The present investigation has raised a number of questions which can be answered only by further research. Among other things, the probability that there is compound formation between the guanidine and the protein, or the rubber, is

extremely interesting. The fact that the curves as determined by the acetone-extraction method and by the hydrolysis method approach each other as the cure continues indicates that it is the bound guanidine that is being destroyed. It seems quite possible that the greater part of the accelerating effect on vulcanization is not due to the guanidine itself but to an addition product of guanidine and an ingredient of crude rubber. In any case, the author believes that further work in this direction will throw considerable light on the mechanism of acceleration.

Acknowledgment

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Change of Penetration with Temperature of Various Asphalts

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THE susceptibility of asphalts to temperature changes is probably the most important characteristic of these substances. To be able to evaluate this coefficient with precision is most essential both for purposes of identification and for revealing intrinsically the suitability of a given asphalt for a desired purpose. Though many attempts have been made to arrive at some method of determining this factor of susceptibility, no satisfactory procedure has as yet been worked out (5).

Abraham (1) observed that the difference in consistometer hardness at 46.1° and 0.0° C. (115° and 32° F.) divided by the Kramer-Sarnow fusing point (2) is a constant for all asphalts derived from the same source. This series of constants he terms "susceptibility factors." Whatever the technical objections to this method may be, these factors do not evaluate the susceptibility to temperature change of those asphalts which come from the same source but which are processed differently, nor does this method yield a definite relation between the true susceptibility and the group factors obtained.

The procedure generally adopted by asphalt technologists consists of obtaining a ratio of the difference between two penetrations at 46.1° and 0.0° C. (115° and 32° F.) divided by that at 25° C. (77° F.). The three penetration readings are obtained with three different loads and two different time periods (3). That this method is not satisfactory is conceded; although it is found useful for identification purposes, it is at times misleading.

Many other methods are in vogue (6). None of these, however, determines any intrinsic property of asphalts. Frequently the order of these various indexes is not the same as the order of the true susceptibilities, while the numerical relation between their magnitude is hardly ever the same as the relative susceptibilities for a series of asphalts. Perhaps the susceptibility of some other property of asphalts to temperature changes may be of greater utility (5), but the

In this investigation a simple equation, $p = A + B \times C'$, was found to express the variation of the penetration of thirteen asphalts with the temperature.

Several sources and methods of processing are represented in the asphalts which were studied. The equation can be solved when three penetrations obtained with the same weight and for the same period of time at different temperatures are known. By means of this equation a simple index, $p_2 - p_1$, was found to represent adequately the order and the relative magnitude of the temperature susceptibility of the thirteen asphalts.

penetration still remains to be the best known and most generally used test for asphalts (4).

The aim of this investigation was not merely to find a factor or an index which would give the relative order of the susceptibilities of different asphalts, but also to obtain a concise expression by means of which the entire curve could be visualized or determined—i. e., the susceptibility of the penetration, dp/dt , at any desired point within a given range of temperature.

The equation suggested below represents experimental data well within the experimental error and gives a concise method of representation. By means of this equation, when three penetrations at three temperatures are known, it is possible to calculate with precision the entire susceptibility curve. Furthermore, an "index" of this susceptibility, yielding relative values over a desired temperature range with adequate precision for all practical purposes, is derived from this equation.

Experimental Procedure

The standard procedure (3) for measuring penetrations was employed. Great care was observed with regard to such important and well-known details as overheating, aging, etc.

A large bath, the temperature of which was varied and controlled, supplied a stream of water within which the cup, filled with the asphalt under investigation, was immersed. A thermometer was imbedded in the asphalt in the center of the cup. Preliminary studies showed that the temperature in the center of the cup and that 1.25 cm. (0.5 inch) away were identical, and that the presence of the thermometer did not affect the penetrometer readings taken half-way between the center and the side of the cup. The cups were allowed to remain at a constant temperature for 30 minutes before a reading was taken, and the thermometer was read before and after each set of readings. No variation larger than 0.2° C. was allowed. In determining the final value of the penetra-

tion at least five readings were taken, the average deviation of which, from the average, did not exceed 0.3 mm.

Thirteen asphalts, the characteristics of which are given in Table I, have been studied, including asphalts from Venezuelan and Midcontinent asphaltic base petroleum as well as native Trinidad Lake. Various processes of manufacture are represented: air-blown, steam-refined, and vacuum-refined.

TABLE I. CHARACTERISTICS OF ASPHALTS STUDIED

Asphalt No. ^a	Source	Process	Penetration ^b	Softening Point B & R ^c
1	Mexican and Texas	Air and steam	7	298
2	Mexican and Texas	Air and steam	11	245
3	Mexican and Texas	Air and steam	11	232
4	Trinidad Lake	Native	2	200
5	Venezuelan	Vacuum-distilled	8	170
6	Midcontinent	Air-blown	25	176
7	Mexican and Texas	Air and steam	26	193
8	Mexican and Texas	Air-blown	30	168
9	Venezuelan	Air-blown	26	169
10	Venezuelan	Vacuum-distilled	26	133
11	Fluxed refined Trinidad Lake	Batch steam	50	131
12	Venezuelan	Vacuum-distilled	42	119
13	Mexican	Steam-refined	220	96

^a These numbers refer to the curves in Figures 1, 2, and 3.

^b At 77° F., 100-gram weight, 5 seconds.

^c Ball-and-ring method.

Change of Penetration with Temperature

The experimental data plotted against the temperature gave a group of smooth curves (Figure 1). The general similarity and nature of the curves suggested that some exponential

equation should express the penetration of all asphalts. Equation 1 was found to represent the experimental results with a high degree of accuracy.

$$p = A + B \times C^t \quad (1)$$

where p is the penetration in decimillimeters

t is the temperature in degrees Centigrade

A , B , and C are constants characteristic of each asphalt

The validity of the equation is proved by plotting $\log(p - A)$ against t . Straight lines are obtained (Figure 2). The equation is further tested by comparing the calculated values with those obtained experimentally. These compared values are given in columns 2 and 3, and 6 and 7 of Table II. The deviations in columns 4 and 8 are in only a few cases greater than 0.4 mm., and in terms of percentage the average deviation is less than 5 per cent.

Three penetrations at any three temperatures are sufficient for the solution of Equation 1. However, a simplification of the solution is gained if the three temperatures are so chosen that

$$t_3 - 2t_2 + t_1 = 0 \quad (2)$$

If 0° C. is taken for t_1 , Equation 1 reduces to the simple form

$$\frac{p_3 - p_2}{p_2 - p_1} = C^{t_2} \quad (3)$$

The values of the three constants calculated for thirteen asphalts are given in Table III. In calculating these con-

TABLE II. COMPARING EXPERIMENTAL AND CALCULATED VALUES AS A PROOF OF VALIDITY OF EQUATION 1

TABLE 11. COMPARISON OF PENETRATION TESTS												
Temp. ° C.	Penetration ^a		Devia- tion	Temp. ° C.	Penetration ^a		Deviation	Temp. ° C.	Penetration ^a		Deviation	
	Expt.	Calcd.			Expt.	Calcd.			Expt.	Calcd.		
Asphalt 1												
0.0	4	4.0	0.0	38.5	10.5	10.2	-0.3	0.0	11.5	11.5	0.0	
22.5	6	6.2	+0.2	42.5	12.5	12.1	-0.4	5.8	14.5	14.2	-0.3	
26.2	7.5	6.9	-0.6	46.0	14	13.9	-0.1	11.0	18	17.3	-0.7	
32.5	8.5	8.4	-0.1	53.2	19	19.0	0.0	20.0	25	24.6	-0.4	
				Average deviation 2.6%				24.5	29.5	29.6	+0.1	
Asphalt 2												
0.0	5	5.0	0.0	35.0	16	16.2	+0.2	28.0	34	34.2	+0.2	
19.0	9.5	9.2	-0.3	41.0	19.5	20.1	+0.6	29.0	34	35.7	+1.7	
25.0	11.5	11.3	-0.2	44.0	22.5	22.5	0.0	Average deviation 1.7%				
30.0	14	13.5	-0.5	50.0	28	28.2	+0.2	Asphalt 9				
				Average deviation 1.7%				0.0	10	10.0	0.0	
Asphalt 3												
0.0	4.5	4.5	0.0	35.2	17	16.1	-0.9	16.5	18.5	18.1	-0.4	
16.5	8	7.8	-0.2	39.6	20	19.3	-0.7	21.0	21.5	21.9	+0.4	
20.0	9	8.9	-0.1	50.0	29.5	30.0	+0.5	26.0	28	27.3	-0.7	
26.4	11	11.3	+0.3	51.5	32	32.1	+0.1	29.0	31	31.3	+0.3	
				Average deviation 2.2%				30.5	34	33.6	-0.4	
Asphalt 4												
0.0	1	1.0	0.0	47.6	13	13.1	+0.1	Asphalt 10				
33.0	3	3.3	+0.3	50.0	17	16.9	-0.1	0.0	4.5	4.5	0.0	
38.0	5	5.0	0.0	51.7	21	20.3	-0.7	17.8	15	14.8	-0.2	
43.7	8.5	8.8	+0.3	55.0	31	29.1	-1.9	24.1	24.5	24.3	-0.2	
				Average deviation 3.0%				27.2	30	31.2	+1.2	
Asphalt 5												
0.0	3.5	3.5	0.0	39.8	21	21.5	+0.5	31.2	42	43.5	+1.5	
18.0	6.5	5.9	-0.6	43.5	29.5	28.3	-1.2	Asphalt 11				
23.2	7.5	7.5	0.0	44.5	31	30.5	-0.5	0.0	8	8.0	0.0	
30.0	10.5	11.1	+0.6	47.0	39	36.9	-2.1	10.0	12.5	15.2	+2.7	
34.0	13.5	14.3	+0.8	52.0	55	54.5	-0.5	12.5	16	18.1	+2.1	
39.5	20.5	21.1	+0.6	53.5	57.5	61.4	+3.9	15.9	21.5	23.4	+1.9	
				Average deviation 3.7%				20.7	35	34.0	-1.0	
Asphalt 6												
0.0	9	9.0	0.0	34.6	40.5	38.3	-2.2	24.0	46	44.4	-1.4	
15.0	15.5	16.7	+1.2	37.5	46	43.4	-2.6	28.8	65	65.8	+0.8	
20.0	19	20.6	+1.6	44.0	60	57.5	-2.5	Asphalt 12				
22.0	22	22.4	+0.4	45.6	64	61.6	-2.4	0.0	5	5.0	0.0	
25.2	25.5	25.6	+0.1	48.0	69	68.4	-0.6	14.0	12.5	12.7	+0.2	
29.5	32	30.8	-1.2	50.0	73.5	74.5	+1.0	20.0	22	22.9	+0.9	
33.0	36.5	35.8	-0.7	52.5	82	83.5	+1.5	23.2	34	32.3	-1.7	
				Average deviation 3.4%				Average deviation 3.0%				
Asphalt 7												
0.0	11	11.0	0.0	41.3	53.5	53.8	+0.3	Asphalt 13				
19.0	20	20.0	0.0	44.0	61	61.5	+0.5	0.0	33	33.0	0.0	
24.5	25	25.0	0.0	46.2	68.5	68.7	+0.2	5.7	50	50.8	+0.8	
27.0	28	27.8	-0.2	49.0	79	79.2	+0.2	9.2	66	66.8	+0.8	
30.0	32	31.7	-0.3	51.5	90.5	90.0	-0.5	13.0	86	90.6	+4.6	
34.0	37.5	38.0	+0.5	54.0	102.5	102.5	0.0	Average deviation 1.9%				
36.7	43	43.1	+0.1	55.3	112	109.6	-2.4	Asphalt 13				
				Average deviation 0.6%				0.0	14.8	100.5	104.8	+4.3
Average deviation 0.6%												

^a 100-gram weight on needle 5-second time period.

^a 100-gram weight on needle 5-second time period.

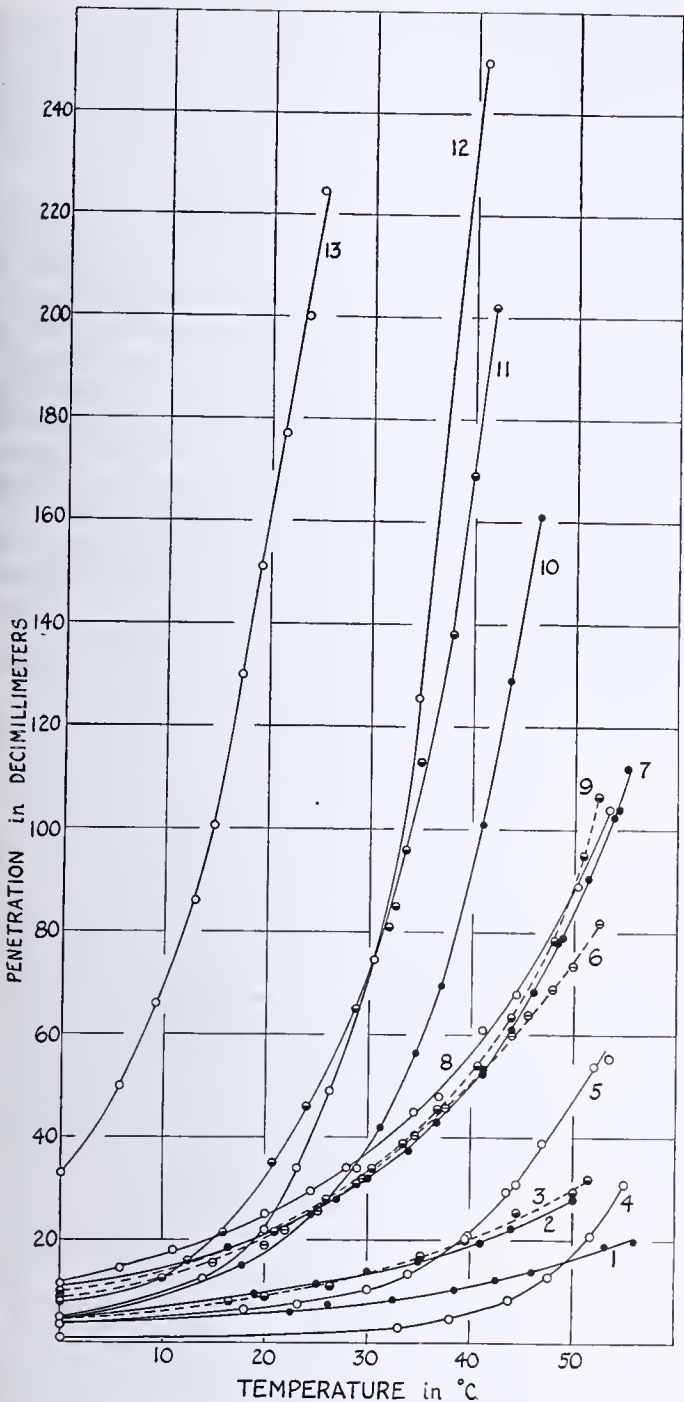


FIGURE 1. EXPERIMENTAL DATA PLOTTED AGAINST TEMPERATURE

consequence of the authors' particular empirical equation, can be obtained from the nature of the experimental curves given in Figure 1. These are not straight lines, nor do they exhibit uniform curvature. Any attempt, therefore, to express the susceptibility of the penetration to temperature changes by a constant factor cannot possibly yield an accurate representation of the true property. The rate of change is different at different temperatures and this difference is not the same for any two asphalts.

TABLE III. CONSTANTS OF EQUATION 1 FOR VARIOUS ASPHALTS

No. of Asphalt	A	B	C
1	3.06	0.94	1.0545
2	1.18	3.82	1.0399
3	1.56	2.94	1.0465
4	0.944	0.056	1.1197
5	2.82	0.68	1.0869
6	0.77	8.23	1.0448
7	6.14	4.86	1.0569
8	2.63	8.87	1.0464
9	4.37	5.63	1.0555
10	1.73	2.77	1.0908
11	2.80	5.20	1.0905
12	3.31	1.69	1.1302
13	4.57	28.43	1.0889

Thus, observing the experimental curves in Figure 1, we note that in the case of Trinidad Lake asphalt (No. 4) the penetration hardly changes with the temperature up to 30° C., while above that temperature the penetration begins to rise very rapidly. The other extreme is shown in the case of asphalt 13, the penetration of which begins to rise rapidly even at the lowest temperature. Asphalt 7 and several others, on the other hand, give an even rise throughout the entire range.

These facts are not revealed by any one constant factor, whereas an accurate representation of fact can be gained by the derivative dp/dt . Or, to conform to the usage of expressing similar variations of other important characteristics of matter, such as the coefficient of compressibility, etc., we may define the susceptibility of asphalts by the coefficient

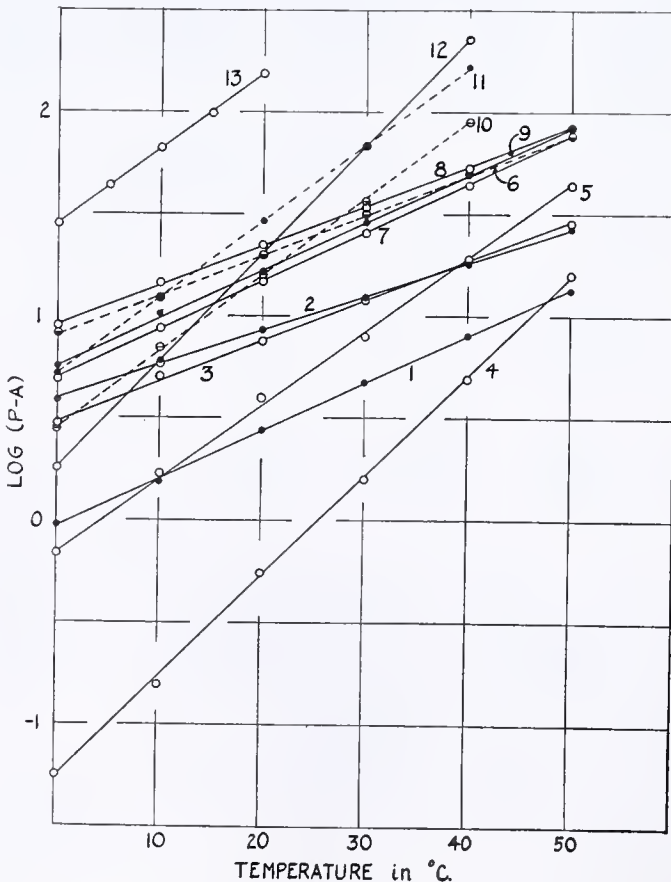


FIGURE 2. DEMONSTRATING VALIDITY OF EQUATION $p = A + B \times C^t$

stants, penetrations were read off the experimental curve at 0.0°, 25°, and 50° C. (32°, 77°, and 122° F.) for all asphalts but Nos. 10, 11, 12, and 13. For asphalts 10, 11, and 12 the temperatures 0.0°, 20°, and 40° C. were used, and for asphalt 13 the temperatures 0.0°, 10°, and 20° C.

Constants B and C can be calculated or read off the curve of $\log (p - A)$ vs. t (Figure 2). The slope of the straight line is $\log C$, and the intercept with the ordinate is $\log B$.

In plotting the straight lines of Figure 2, penetrations at round temperatures were read off experimental curves (Figure 1).

It may be of interest to point out that B is a dimensional constant, so that any temperature scale can be employed by modifying B correspondingly. Relation 2, however, will be changed.

Susceptibility to Temperature Changes

Differentiating Equation 1 we obtain $dp/dt = B \times \ln C \times C^t$. It follows that neither the first nor any other derivative is a constant. A further proof, however, that this conclusion is an inherent property of the penetration and not merely a

$1/p \times dp/dt$. Values of dp/dt for the thirteen asphalts at four different temperatures are given in Table IV.

TABLE IV. SUSCEPTIBILITIES AT FOUR DIFFERENT TEMPERATURES

No. of Asphalt	dp/dt , 0° C.	dp/dt , 25° C.	dp/dt , 46.1° C.	dp/dt , 50° C.
1	0.05	0.19	0.58	0.72
2	0.15	0.40	0.91	1.05
3	0.13	0.42	1.08	1.30
4	0.006	0.43	1.15	1.80
5	0.06	0.46	2.63	4.30
6	0.36	1.07	2.72	3.23
7	0.27	1.07	3.43	4.23
8	0.40	1.24	3.23	3.87
9	0.30	1.17	3.65	4.50
10	0.24	2.56	13.3	..
11	0.45	3.98
12	0.21	4.35
13	2.42

Index of Susceptibility

If a practical simplification is desired for the sake of conciseness, it is possible to obtain a constant which will express approximately the relative susceptibilities of different asphalts. This can be obtained by evaluating the area under the curve of dp/dt vs. t (Figure 3). This area is given by integrating the differential with respect to temperature between the limits of the desired temperatures.

Index of susceptibility = area under curve dp/dt vs. t

$$= \int_{t_1}^{t_2} \frac{dp}{dt} dt = p_2 - p_1 \quad (4)$$

Thus we obtain not only a constant to express the relative susceptibilities of various asphalts, but the entire problem is a good deal simplified. Only two penetrations at specified temperatures are necessary. It must be borne in mind that in comparing the indexes of different asphalts the temperature range in all cases must be the same. In columns 2, 3, and 4 of Table V are given the values of such indexes obtained by integrating between 0° and 25° C., 0° and 40° C., and 0° and 50° C., respectively.

TABLE V. INDEXES OF SUSCEPTIBILITY

No. of Asphalt	$\int_0^{25} \frac{dp}{dt} dt$	$\int_0^{40} \frac{dp}{dt} dt$	$\int_0^{50} \frac{dp}{dt} dt$
4	0.9	5.1	15.9
1	2.6	7.0	12.4
2	6.3	14.4	23.1
3	6.2	15.2	25.9
5	4.8	18.3	43.1
6	16.4	39.4	65.5
7	14.5	39.5	72.3
9	16.1	43.2	78.1
8	18.7	45.5	76.7
10	21.6	87.0	..
11	40.1	160.9	..
12	34.4	224.6	..
13	191.5

The order of the susceptibilities is not the same in the three columns. This should be expected because of the change in the temperature range, since some asphalts are more susceptible than others at one part of the temperature range and less susceptible at another part of it.

It might seem superficially that the slope of the straight lines in Figure 2, which is equal to $\log C$, could serve as an index. Or, since $dp/dt = B \times \ln C \times C^a$, the product $B \times \ln C$ could be used as a factor of the susceptibility. Neither, however, gives a series of constants which represent the order of the true susceptibilities as noted in Figures 1 and 3.

In the early stages of this investigation the authors were hopeful that the slopes of the straight lines (Figure 2) could be utilized as indexes of the susceptibility. However, as the work progressed and a larger variety of asphalts were included, it became obvious that these slopes were not true indicators of the relative susceptibilities.

In column 2, Table VI, are given the values of $\log C$, the slope of the respective straight lines, multiplied by 100. Comparing these values with the obvious susceptibilities as seen, if only qualitatively, by the experimental curves (Figure 1), it will be noted that neither the true order nor the relative magnitudes are represented. Thus the slope for asphalt 13 can be given as 8.52. This is considerably smaller than the values of the slopes of asphalts 12 and 4, which are 12.24 and 11.31, respectively. Yet it is obvious that susceptibility of asphalt 13 is by far the greatest, while the susceptibility of asphalt 4 is one of the smallest. The slopes of asphalts 10, 11, and 13 are practically equal—viz., 8.69, 8.66, and 8.52, respectively—yet their respective susceptibilities are far apart.

The product $B \times \ln C$ given in column 3, Table VI, is a much better approximation. But comparing these values

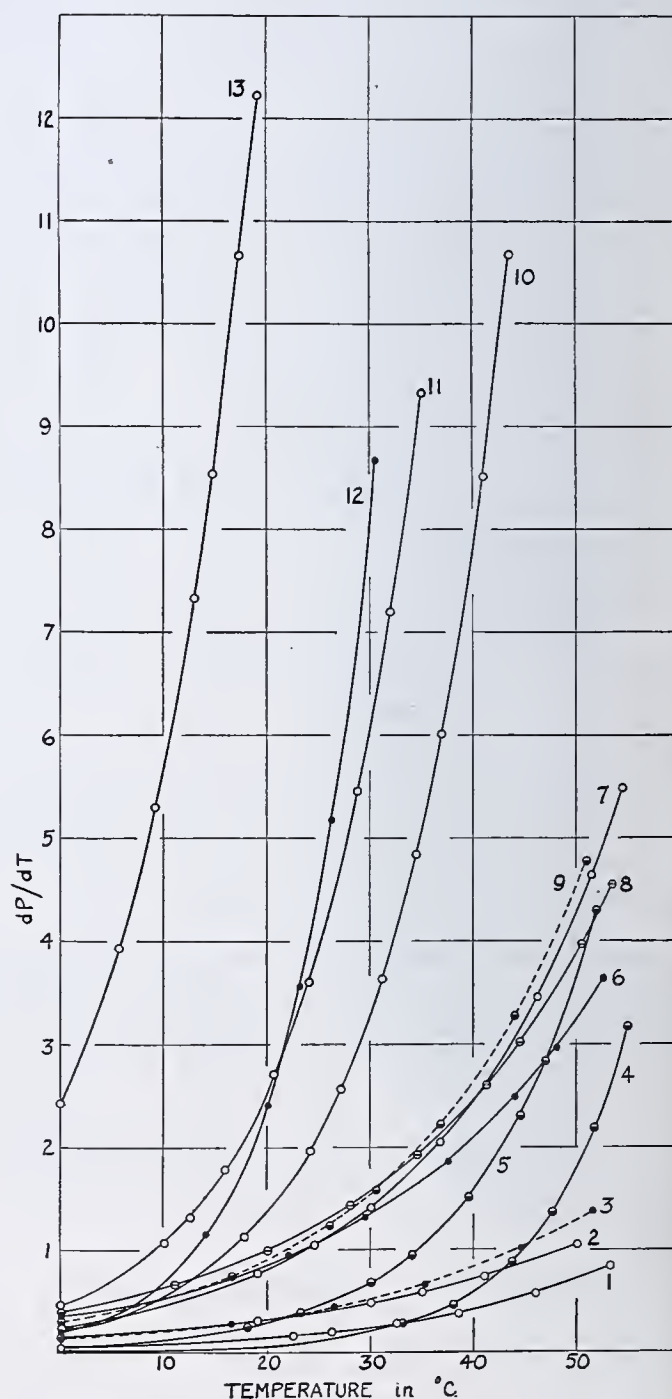


FIGURE 3. INDEX OF SUSCEPTIBILITY

with the values of dp/dt at the several temperatures (Table IV) it will be seen that the order of the susceptibilities is not quite correct in a few cases.

Since it is customary to express the susceptibility as some sort of ratio which involves the actual penetration in addition to the change in penetration, it was suggested that the index $p_2 - p_1$ be divided by the penetration at a given temperature. Such ratios are valid only when similar types of asphalts are compared. However, discordant results are obtained when a large group of asphalts are compared.

It is felt, therefore, that the index suggested, $p_2 - p_1$, as an approximation, is superior to any others. The value of dp/dt , however, is the only accurate guide for classifying the susceptibilities of large varieties of asphalts.

TABLE VI. VALUES OF LOG C, THE SLOPE OF THE STRAIGHT LINES (FIGURE 2) AND B ln C

No. of Asphalt	Log C × 10 ²	B ln C × 10 ³
4	11.31	5.32
1	5.31	4.98
2	3.91	14.93
3	4.55	13.34
5	8.33	5.66
6	4.38	36.04
7	5.53	26.86
9	5.40	30.36
8	4.53	40.19
10	8.69	23.46
11	8.66	45.00
12	12.24	20.66
13	8.52	241.87

Effect of Weight upon Penetration

The above discussion refers to penetrations obtained with a needle loaded with the same weight (100 grams) and for the same interval of time. It may be desirable at times to employ different weights. Thus in the case of a very hard asphalt, such as No. 4, the penetration is so small that the magnitude of the error inherent in the experimental procedure becomes appreciable and a larger reading is desirable. On the other hand, in case of very soft asphalts, such as No. 13, the penetration is too great when obtained with 100 grams and a weight of 50 grams may be more suitable.

To determine the relation between weight and penetration, a series of readings was made using different weights. Several asphalts were studied. It was found that in all cases the ratio of two penetrations obtained with two different weights was practically constant over the entire temperature range. The experimental results are given in columns 2, 3, 4, and 5 of Table VII. In columns 6, 7, and 8 are given the ratios of penetration obtained with three different weights. This fact can be utilized whenever it is desirable to measure penetration with a weight smaller or larger than 100 grams.

The index then for a soft asphalt is

$$(p_{50g.}/5 \text{ sec.}/40^\circ \text{ C.} - p_{50g.}/5 \text{ sec.}/0^\circ \text{ C.}) \times \frac{p_{100g.}/5 \text{ sec.}/0^\circ \text{ C.}}{p_{50g.}/5 \text{ sec.}/0^\circ \text{ C.}}$$

or in case of a hard asphalt

$$(p_{200g.}/5 \text{ sec.}/40^\circ \text{ C. or } 50^\circ \text{ C.} - p_{200g.}/5 \text{ sec.}/0^\circ \text{ C.}) \times \frac{p_{100g.}/5 \text{ sec.}/40^\circ \text{ or } 50^\circ \text{ C.}}{p_{200g.}/5 \text{ sec.}/40^\circ \text{ or } 50^\circ \text{ C.}}$$

The accuracy of this conversion will depend upon the constancy of the ratio of the two penetrations throughout the temperature range.

As practical illustrations of the possible deviation we can calculate the index for a hard asphalt, No. 4, and a soft asphalt, No. 10, using the data given in Table VII.

For No. 4,

$$\text{Index} = p_{100g.}/5 \text{ sec.}/50^\circ \text{ C.} - p_{100g.}/5 \text{ sec.}/0^\circ \text{ C.} = 17 - 1 = 16$$

or

$$\text{Index} = (p_{250g.}/5 \text{ sec.}/50^\circ \text{ C.} - p_{250g.}/5 \text{ sec.}/0^\circ \text{ C.}) \times \frac{p_{100g.}/5 \text{ sec.}/50^\circ \text{ C.}}{p_{250g.}/5 \text{ sec.}/50^\circ \text{ C.}} = (33.4 - 2) \frac{17}{33.4} = 15.98$$

In the case of a soft asphalt, accepting for the sake of illustration 25.8° C. as the upper temperature limit, for asphalt No. 10,

$$\text{Index} = p_{100g.}/5 \text{ sec.}/25.8^\circ \text{ C.} - p_{100g.}/5 \text{ sec.}/0^\circ \text{ C.} = 29.5 - 4.5 = 25.0$$

or

$$\text{Index} = (p_{50g.}/5 \text{ sec.}/25.8^\circ \text{ C.} - p_{50g.}/5 \text{ sec.}/0^\circ \text{ C.}) \times \frac{p_{100g.}/5 \text{ sec.}/0^\circ \text{ C.}}{p_{50g.}/5 \text{ sec.}/0^\circ \text{ C.}} = (20 - 3) \frac{4.5}{3} = 25.5$$

The agreement in both cases is excellent.

Conclusion

An equation is found which expresses concisely the variation of the penetration of various asphalts with temperature. The equation represents the experimental data for thirteen asphalts of different sources and methods of processing, well within experimental error. The present technic followed by routine asphalt laboratories of reporting penetrations at three different temperatures is found sufficient for solving the equation

$$p = A + B \times C^t$$

providing the weight and time period for all three penetrations are the same and the temperatures expressed in Centigrade are so chosen that

$$t_3 - 2t_2 + t_1 = 0$$

i. e., 50°, 25°, and 0° C., or 40°, 20°, and 0° C. This limitation is not essential for the solution of the equation, but the solution is simplified a good deal if the suggestion is followed.

By means of this equation it is possible to represent the change of penetration with temperature throughout the working temperature range. The differential dp/dt represents the true susceptibility. However, to conform to the usage of expressing similar variations of other important character-

TABLE VII. EFFECT OF WEIGHT UPON PENETRATION

Temp. ° C.	Penetrations				Penetration Ratios		
	50 g.	100 g.	200 g.	250 g.	100/50	100/200	100/250
Asphalt 8							
0.0	5.0	9.0	14.0	16.0	1.80	0.653	0.562
20.0	14.5	24.8	36.2	41.2	1.71	0.685	0.602
25.0	17.5	30.0	44.5	51.4	1.71	0.674	0.583
30.0	20.9	36.3	54.7	65.0	1.74	0.663	0.558
35.0	25.6	45.2	68.2	84.0	1.76	0.663	0.538
40.0	31.8	56.4	1.74
					Av. 1.74	0.677	0.568
Asphalt 4							
0.0		1.0	..	2.0		..	0.5
30.0		2.5	4.6	5.8		0.54	0.43
35.0		3.6	7.0	8.0		0.51	0.45
40.0		6.0	11.6	13.3		0.517	0.451
45.0		10.1	18.1	21.6		0.559	0.467
27.0		17.0	27.3	33.4		0.623	0.509
						Av. 0.550	0.468
Asphalt 6							
0.0	4.5	7.0	11.0	12.0	1.55	0.636	0.583
25.8	17.0	25.5	40.5	46.0	1.50	0.603	0.550
Asphalt 9							
0.0	5.5	9.0	13.5	16.0	1.63	0.666	0.563
25.8	17.5	28.0	45.5	51.0	1.60	0.615	0.550
Asphalt 10							
0.0	3.0	4.5	7.0	8.5	1.5	0.643	0.529
25.8	20.0	29.5	49.0	56.5	1.48	0.602	0.522

istics of matter, such as the coefficient of compressibility, etc., we may define the susceptibility of asphalts by the coefficient $1/p \times dp/dt$. This can be advantageously used for classification of all asphalts, regardless of their sources or methods of processing, providing the above empirical equation, or a similar equation, expresses the experimental variation of the penetration with temperature.

Unfortunately, this coefficient is not a constant. The established usage of asphalt laboratories is to employ some sort of a constant factor for the classification of asphalts. The numerous methods of deriving these factors are no doubt found useful by the laboratories using them, and some laboratories find one factor more useful than another. None of these factors, using penetration as a basis, represents the true susceptibility, though for limited groups of asphalts the representation is no doubt sufficient for practical purposes, especially since such factors are employed primarily for purposes of identification rather than classification.

The authors suggest, therefore, as an approximation, a constant factor to represent the susceptibility, the definite integral of dp/dt between the limits of the desired temperature. This integral is equal to $p_2 - p_1$. It is found that this factor represents the true order of the susceptibilities and, approximately, the relative magnitudes of all asphalts studied in this investigation. Several other possible expressions

which suggested themselves were found to be of no intrinsic value.

It is further shown that the ratio of penetration obtained with different weights at different temperatures is practically constant. This makes it possible to use penetration of a hard asphalt obtained with 200 or 250 grams and that of a soft asphalt with 50 grams and the respective indexes are nevertheless rigorously comparable.

Acknowledgment

The authors wish to thank R. N. Traxler of The Barber Asphalt Company for many valuable suggestions and criticisms.

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Determination of Nitric Oxide in Coke-Oven Gas

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ABOUT six or seven years ago the problem of stoppages in small orifices of gas distribution systems began to become acute. Investigation soon showed that minute amounts of organic nitro compounds were responsible for a considerable portion of this trouble. The original general theory was that nitric oxide (NO) formed in the combustion gas of the oven flues and perhaps elsewhere found its way through the oven walls into the gas, slowly oxidized to nitrogen peroxide, and combined with unsaturated hydrocarbons present in the gas to form gummy deposits in the distribution system.

It was found that the amounts of gum involved were almost unbelievably small, and that therefore no simple method of determination, such as filtering and weighing, was likely to be successful. The fact that a distinctly ultrasensitive method was needed sharply limited procedure. It was perhaps fortunate, however, that derivatives of nitrous acid were involved, since delicate color tests for this substance were well known and are among the most sensitive chemical tests available to the analyst. Therefore, the analytical attack was made against the nitro group.

Tropsch and Kassler (5) suggested introducing the gas into a large flask together with a large fraction of oxygen, and adding caustic soda solution which was later added to an acetic acid solution of an amine, such as Griess-Ilosvay reagent. The whole was shaken for 20 minutes and the color produced in the solution compared with standards. This was cumbersome and had the distinct disadvantage that the largest feasible size of sample was so small that the method was of practical value in only a few cases where the concentrations of nitric oxide were relatively high.

Shortly after this Schuftan (2) published a dynamic method in which the gas was scrubbed with potassium hydroxide solution, dried with potassium hydroxide pellets, mixed with one-half its volume of oxygen, passed through a delay bottle for an interval of 15 minutes, and then scrubbed with a solution

of *m*-phenylenediamine (diaminobenzene) in dilute acetic acid. The color formed was a measure of the nitric oxide present.

This was a distinct improvement over the other methods. The size of sample was substantially unlimited and the shaking entirely eliminated by this procedure. Since only a fraction of the nitric oxide present was recovered, for both of these methods a reference curve was employed, apparently based upon the calculations of Bodenstein or upon direct calibration of nitric oxide-nitrogen mixtures. So far as the writer is aware, not many data have been presented for nitric oxide recovery based upon small known additions of nitric oxide to nitric oxide-free coke-oven gas.

Fulweiler (1) has described a modification of the Schuftan dynamic method which involves mixing the gas with an equal volume of oxygen, allowing the mixture to react for approximately 1.5 minutes, and then absorbing the nitrogen tetroxide (NO₂) formed directly in Griess reagent. He claims that there is a catalyst present in manufactured gas that accelerates the conversion of nitric oxide into nitrogen tetroxide. Later Fulweiler extended the application of this method to a continuous recording instrument for the determination of nitric oxide in gas.

Tests by the writer upon nitric oxide in nitrogen showed a very fair agreement with the Schuftan curve. This reference curve shows a marked variation in the amount of recoverable nitric oxide, depending upon the concentration of the nitric oxide originally present in the gas. Where there is a nitric oxide concentration of several hundred parts per million the correction factor is substantially unity. For 10 p. p. m. it is about 10, for 1.0 p. p. m. it is about 200, etc.

When the author's work was started on coke-oven gas it was apparent that this nitrogen curve did not apply. As an actual matter of fact, the particular method subsequently standardized by the writer for use on coke-oven gas shows a

factor of very approximately 2 for all concentrations of nitric oxide tested.

This difference made a fundamental study of analytical methods a matter of first importance. A survey of available lines of attack seemed to indicate that the most profitable procedure would be to continue along the lines of Schuftan's initial effort.

One of the most difficult problems connected with the search was the preparation of a synthetic sample of known nitric oxide concentration. This involved the production of a nitric oxide-free gas. Since the composition of the gas had a marked effect upon the nitric oxide recovery as shown by the author's experience with nitrogen, it seemed that the least possible treatment of the gas to remove nitric oxide was the best. Chemical treatment in particular was open to question, especially since so little was known at the start about the chemical properties of the substances involved.

The method finally adopted for producing nitric oxide-free gas consisted in compressing the gas containing about 0.5 per cent of oxygen to 2.1 kg. per sq. cm. (30 pounds per square inch) gage pressure and allowing it to stand several hours, usually overnight.

A cylindrical pressure-tank having about 0.5 cu. m. (17 cubic feet) displacement was set up outside the building, and was connected to the gas main on the pressure side of the plant gas booster. Oxygen was added in the form of air before the tank was opened to the line pressure. After collecting the sample, the inlet valve was closed and the pipe connecting it to the gas main was vented to the air (as shown in Figure 1) to prevent any possible contamination of the sample with untreated gas. A Schuftan test of 7 hours' duration run upon gas treated in this manner gave a zero blank. It was therefore considered that this part of the problem had probably been solved.

The next step involved the addition of small known amounts of nitric oxide to this gas. The concentrations in which the author was interested were seldom greater than 1 p. p. m. and sometimes one one-hundredth of this. Since the author's apparatus used about 0.03 cu. m. (1 cubic foot) of gas per hour, this meant a distribution into the gas during a period of 1 hour of not more than 0.03 ml. of pure nitric oxide gas. Owing to the necessity of especially preparing a nitric oxide-free gas, there were distinct limitations upon the amount of gas it was practical to waste. On the other hand the nitric oxide could not be diluted with nitrogen with impunity because of the traces of oxygen that this gas usually contains and which would react with some of the nitric oxide. Therefore, while in actual operation the figure of 0.03 ml. of nitric oxide per hour was increased somewhat by dilution, etc., the additions of nitric oxide-bearing gas to the main gas stream were seldom more than 0.1 to 0.2 ml. per hour and

sometimes much less. A flow sheet of the apparatus used in making this synthetic sample appears in Figure 1.

The gas impounded in tank *A* at 2.1 kg. per sq. cm. (30 pounds per square inch) gage pressure, as previously described, passes through the service governor, *B*. This is a weight type, "pounds-to-inches" governor. After passing the point of nitric oxide enrichment in the manifold, *J*, the gas is mixed as shown in an empty 19-mm. (0.75-inch) test tube, *M*. Immediately following this mixing, an aliquot is withdrawn for analysis. It was originally hoped that the gas could then be simply passed through a seal, measured, and wasted. However, this nitric oxide metering apparatus requires constancy of flow and constancy of pressure of a fairly high order throughout the period of the test, and the nearer the pressure is to that of the atmosphere the better the results obtained. A change of 2.5 mm. (0.1 inch) of water pressure at *L* has a marked effect on both gas rates. With the pressure at *A* varying from 30 pounds or more down to a few inches of water, the gas governor could not quite meet the requirements.

The combination *N*, *P*, *R* was, therefore, designed and installed. *N* is an ordinary 0.1-cu. foot wet test meter. The large indicating hand and meter shaft are soldered to the low-speed shaft of a worm-type reducing gear (200 to 1 ratio). The high-speed shaft of the reducer is directly connected to the shaft of a synchronous motor taken from a Saja pump, such as is used with aquariums. Since these meters have only about a 13-mm. (0.5-inch) water seal, the water in the meter was adjusted to a point slightly above its normal level to provide a somewhat greater margin of safety. After *N*, the gas passes through a water seal, *S*, and is wasted through a 0.1-cu. foot wet test meter not shown in Figure 1. The water level in *S* can be adjusted by means of tube *T* and cock 16. At the start the gas is turned into the line and the water level in *S* adjusted so that the amount of gas passing through *N* (with motor running) as shown by the waste gas meter reading is approximately equal to the amount that would normally pass through *N* if the meter were traveling at this speed under normal metering conditions. For this mechanical setup the speed was fixed at 1.7 liters (0.06 cu. foot) per minute. The net effect obtained then is that the meter *N* at the start is running approximately free or perhaps actually slightly impeding the gas flow; but as the pressure dies down during the run, the meter tends to pick up the load slightly. At intervals during the operation the waste meter is timed and factors calculated for *N* to arrive at a measure of the correct gas flow. These factors indicated that during a period of 4 hours the line pressure gradually dropped 5 to 8 mm. (0.2 to 0.3 inch) but giving a drop of only 2 or 3 per cent in gas flow.

The bottom of the system *D*, *G*, *K* is sealed with pure dry mercury. *D* is a glass tube 5 cm. (2 inches) in diameter and about 2.1 meters (7 feet) long. *G* is a 1-ml. pipet (Bureau of Standards certified) having a graduated scale about 18 cm. (7 inches) long and divided into 100 parts. It is therefore possible to read the scale to 0.001 ml. with fair accuracy from a mechanical standpoint. The capacity of the tube at a large number of points was determined gravimetrically and compared with the Bureau of Standards' delivery calibration. The accuracy of the scale was found to be well within the over-all accuracy of the work. The buret, *G*, is sealed into the system as shown. The capacity of the unknown gas volume at the top enclosed between the top of the scale and cocks 13 and 14 was determined for use in calculating the effect of temperature and pressure changes on the volume of nitric oxide delivered to *J*. *F* is a water jacket; *H* is a thermometer; *K* is a pressure-compensating device; *L* is a water-filled manometer. The top of *G* above cock 14 is 1-mm. capillary tubing, drawn down at the tip to a microscopic opening. In this instance the orifice was 0.01 mm. in diameter or less as determined by microscopic measurement. This provided a linear velocity for the nitric oxide at the tip sufficient to prevent diffusion of the coke-oven gas backward into *G*. The diffusion rate of this gas is of the order of magnitude of about 15 cm. per minute under these general conditions. The tip of *G* extends into a somewhat constricted arm of a T leading into the main gas line. Through a side arm a small amount of nitrogen is introduced to carry the nitric oxide definitely and regularly into the gas stream.

The storage tube, *E*, is filled with pure dry nitric oxide prepared in a manner described later, whence it is transferred to flush and to fill *G* as desired. During all tests, cocks 9, 10, 11, and 13 and the contiguous portions of the 2-ml. capillary tubes leading from them are filled with mercury, thus providing a positive gas seal. Care was always taken to keep a slight positive pressure differential on the nitric oxide at all times. During operation the nitric oxide is forced from *G* into *J* by allowing water from the overflow device, *C*, to run slowly down the sides of *D* onto the surface of the mercury. In this manner the apparatus could be run continuously for a period of 7 hours or more.

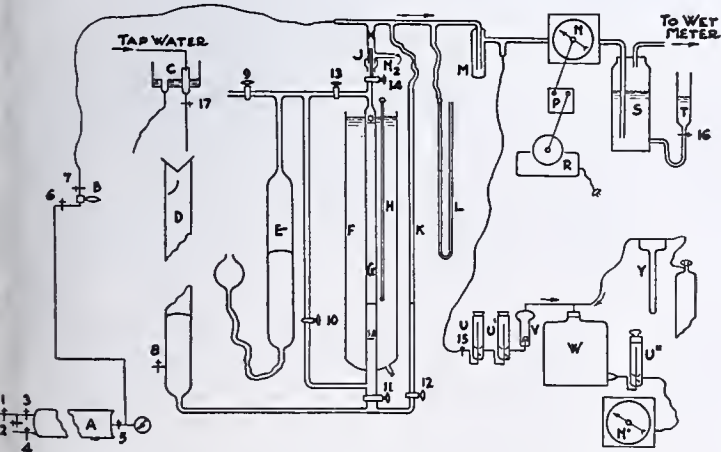


FIGURE 1. APPARATUS FOR MAKING AND ANALYZING SYNTHETIC SAMPLES OF NITRIC OXIDE IN COKE-OVEN GAS

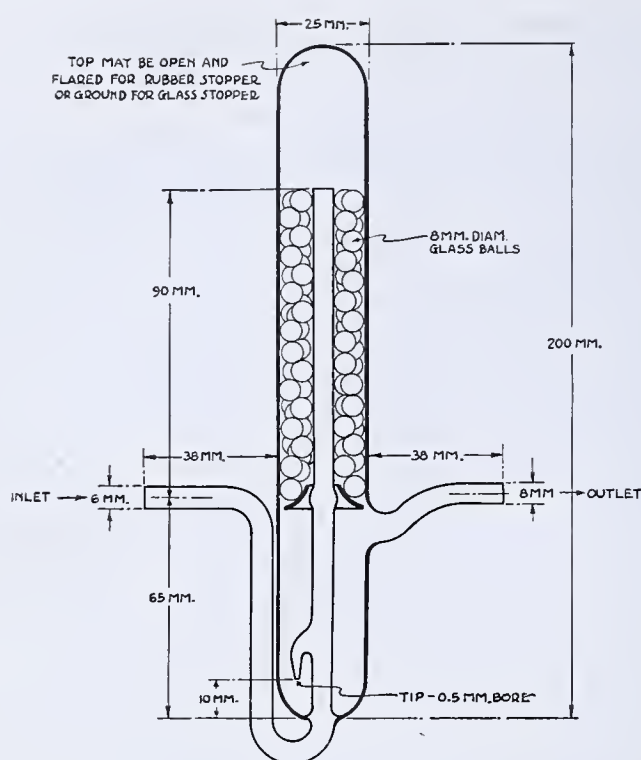


FIGURE 2. ABSORBER WITH LOW BACK PRESSURE

The measurement of nitric oxide added to the gas is accomplished by reading the mercury level in *G* at the beginning and at the end of any test together with the line pressure, barometric pressure, and temperature. The difference between the two corrected gas volumes represents the volume of gas (N. T. P.) forced from *G*. In connection with corrected meter readings and dilution factors, if any, the p. p. m. of nitric oxide in the gas can be calculated with considerable accuracy. The metering apparatus was run under conditions such that the temperature changes rarely amounted to more than 0.5° C. per day. The probable over-all accuracy of the metering apparatus is believed to be about 2 per cent.

For the preparation of the nitric oxide a nitrometer of the DuPont type was used. For the lower range of concentrations the nitric oxide was diluted with nitrogen. It was considered unsafe to use dilutions greater than 1 to 10, and in preparing even these dilutions a special technic was employed. A solution of a known amount of potassium nitrate was prepared and analyzed by means of the nitrometer. A measured amount of nitrogen was then introduced into the clean nitrometer, followed by a measured amount of the potassium nitrate solution and the required amount of sulfuric acid. The nitrometer was then shaken for 2 minutes and allowed to stand for 15 to 30 minutes with occasional shaking. The gas was then ready to transfer to tube *E* of the metering device through cock 9. *E* was always first flushed with nitrogen and then two or three times with the nitric oxide mixture to remove traces of oxygen before the final filling.

After passing through the mixing tube, *M*, the nitric oxide-enriched gas is ready for analysis or other study. Various analysts working separately found it desirable to make changes in the details of the Schuften procedure as originally published. The bubbler tube scrubbers were not satisfactory from an efficiency standpoint and more efficient scrubbers were substituted. Also many analysts felt that the apparatus should be protected from any ammonia that might get into the line at times and which in any considerable quantity would certainly ruin the test. All these changes and additions increased the back pressure on the apparatus until the average Schuften apparatus was operating under 0.10 to 0.15 kg. per sq. cm. (1.5 to 2.0 pounds per square inch) pressure. This usually required a pump which was disadvantageous from several viewpoints.

For these reasons the writer used a scrubbing apparatus which has previously been described by him (3). It is designed especially for removing a very small amount of sub-

stance from a large amount of gas with a small amount of reagent and with a very low operating back pressure [usually less than 13 mm. (0.5 inch) of water]. A sketch of this scrubbing apparatus is shown in Figure 2.

In the lower right-hand corner of Figure 1 is shown a flow sheet of the analytical apparatus as finally designed.

Materials Required

For the operation of this method the following materials will be required:

Apparatus

- 2 Shaw absorbers (3), rubber stopper type
- 1 Shaw absorber (3), glass stopper type
- 1 aspirator bottle, 2-liter capacity, with straight sides, approximately 11.5 cm. (4.5 inches) in diameter \times 18 cm. (7.25 inches) to base of neck. Kimball's "Exax"
- 1 flowmeter, capable of indicating 0.00198 cu. meter (0.07 cu. foot) per hr.
- 1 wet test meter (0.1-cu. foot type)
- 1 set Nessler tubes, tall form, 50-ml. capacity
- 0.5 kg. (1 pound) solid glass balls, 5 mm. (Eimer and Amend catalog No. 17602)
- 1 calcium chloride drying tube 12.5 cm. \times 1.5 cm. (5 \times 0.61 inches) (Eimer and Amend Catalog No. 22532)
- 1 glass tee, 6 mm.
- 3 tool clamps, adjustable spring type (convenient for holding absorbers)
- 1 small gas governor (No. 28, Fisher Governor Company, Marshalltown, Iowa, optional)
- Necessary supports and general laboratory apparatus
- Suggested: 1 iron stand 12.5 \times 20.0 \times 50 cm. (5 \times 8 \times 20 inches) (Eimer and Amend catalog No. 31882); 4 clamps, 22.5 cm. (9 inches) (Eimer and Amend catalog No. 20206); 4 clamp holders (Eimer and Amend catalog No. 20240).

Chemicals

- Sulfuric acid, c. p.
- Potassium hydroxide, c. p., large pellets
- Sodium nitrite (Baker and Adamson analyzed)
- m*-Phenylenediamine (Eastman technical) (1,3-benzenediamine)
- Activated charcoal, Nuchar, powdered
- Oxygen
- Acetic acid, glacial
- Acetone, c. p.

Solutions

- Sulfuric acid, 10 per cent by volume of 95 per cent acid (approximately)
- Potassium hydroxide 30 per cent solution (approximately)

***m*-PHENYLENEDIAMINE REAGENT SOLUTION.** Pour hot water on 5.0 grams of the crystals. Stir to dissolve, add 25 ml. of glacial acetic acid, and dilute to 1 liter. This solution will keep more or less indefinitely in a stoppered bottle. Portions must be clarified with charcoal before use, since light and air slowly cause a darkening of the solution. To clarify, place 300 to 500 ml. in a 1-liter beaker, add about one heaping teaspoonful of Nuchar, heat to above 60° C., but avoid boiling. Stir to wet the charcoal thoroughly, and filter through a free-flowing paper substantially free of nitrite. In starting the filtration fill the paper cone to destroy at once any nitrite residues and allow a generous portion of the Nuchar to pass into the filter. The first filtrate will be cloudy. When it has started to run clear, return the cloudy portion to the original beaker and catch the filtrate in a clean glass-stoppered bottle. Do not wash filter. The solution should be water-white. Keep away from strong direct light. It is suggested that this solution be clarified daily, although the analyst can use his own judgment in this regard. It is simply a matter of color interference that is involved.

STANDARD SODIUM NITRITE SOLUTION. Stock solution, 0.300 gram of sodium nitrite dissolved in exactly 1 liter of distilled nitric oxide-free water. Standard solution, exactly 10.0 ml. of the stock solution diluted to 1 liter with nitrite-free distilled water. This is one-tenth the strength of the solution recommended by Schuften but is more convenient to use. Some analysts add a drop of chloroform to this solution as a preservative. The ultimate standard for this work is silver nitrite (AgNO_2) prepared according to Treadwell and Hall (4).

Mechanical Arrangement of Apparatus

The general idea of the procedure is to pass a known amount of gas through scrubbers containing acid and both liquid and solid alkali, to mix it with a known amount of oxygen (5 per cent in this case) and, after subjecting it to a time delay, to scrub it with an amine and read the color formed.

Accordingly, on a suitable support in series arrangement the two rubber-stoppered absorbers, U and U' (Figure 1), are set up followed by the calcium chloride tube, V , which delivers into a glass T , one end of which is fitted into the top of the 2-liter delay bottle, W , and the other end of which is connected to the oxygen supply. Following the delay bottle the glass-stoppered absorber U'' is placed. This in turn is connected to deliver to the 0.1-cu. foot wet test meter, N' . Oxygen is introduced at the point above mentioned after having been measured by flowmeter Y . The calcium chloride tube, V , is in an inverted position. The large end at the bottom is closed by a rubber stopper carrying a glass lead tube which extends about 25 mm. (1 inch) into the calcium chloride tube beyond the edge of the rubber stopper. The end of the lead tube is shielded by a glass thimble. This makes a simple and effective potassium hydroxide drying tube.

During operation the first scrubber, U , contains 10 ml. of the dilute sulfuric acid plus 2 or 3 ml. of the *m*-phenylenediamine reagent. Scrubber U' contains 15 ml. of the potassium hydroxide solution. The calcium chloride tube contains 5 to 8 cm. (2 to 3 inches) of potassium hydroxide pellets. Bottle W is empty and dry. The glass-stoppered absorber, U'' , contains 10 ml. of the *m*-phenylenediamine reagent solution.

This apparatus may be set up around an ordinary laboratory iron stand with iron clamps, in which case it is readily portable and easily cleaned, or it may be mounted on a board with the bottle in the rear. With the original Schuftan arrangement a large bottle filled with an explosive gas mixture was used and the board was more or less mandatory. The present bottle is much smaller, and the mixture containing only 5 per cent of oxygen is outside the explosive range for this mixture as determined by the United States Bureau of Mines.

Procedure

Gas is turned into the apparatus at such a rate that, when combined with 5 per cent oxygen, it will undergo in the bottle an average delay period of 3 minutes. This represents a flow of about 37.7 liters (1.33 cu. feet) of coke-oven gas per hour and 2 liters (0.07 cu. foot) of oxygen per hour.

Before connecting up the *m*-phenylenediamine absorber, the gas mixture is allowed to flow through the apparatus at least 20 minutes to establish equilibrium.

The absorber, U'' , is then placed in the line, the meter read, and the gas rate adjusted if necessary. The test is allowed to run until a conveniently readable color has developed in the reagent solution in U'' . This time may vary from a few minutes to several hours, depending upon the concentration of nitric oxide in the gas. The absorber is then removed and the meter read. The gas flow through the apparatus is not interrupted between tests. It is suggested that the optimum depth of color is the amount developed by 3 to 5 ml. of the sodium nitrite standard solution (0.003 gram per liter of sodium nitrite).

When the gas scrubbing has been completed, the absorber content is washed into a Nessler tube, diluted to the mark with nitrite-free water, and mixed. It is then compared with a standard tube in the following manner:

Choose a standard tube having a slightly paler color than the unknown tube. Into a roughly calibrated graduated cylinder, remove portions of the unknown solution until the color of the unknown matches the standard. Note the number of milliliters of solution in the unknown tube. Then $\frac{50}{\text{ml. in unknown tube}} \times \text{ml. of sodium nitrite solution in standard tube} = \text{ml. of standard solution equivalent to the color developed in the test.}$

Both the amount of *m*-phenylenediamine and the concentration of acetic acid in these colored solutions are capable of affecting the depth of color. It is therefore recommended that for the final comparisons the tubes compared shall contain the same volume and depth of liquid and the same concentration of reagents.

The standard tube mentioned above is prepared by measuring into it with a Mohr pipet a chosen number of milliliters of the dilute sodium nitrite solution (0.003 gram per liter of sodium nitrite) and following with this 10 ml. of the *m*-phenylenediamine reagent solution. The tube is shaken to mix and let stand about 20 minutes. It is then diluted with nitrite-free distilled water to the mark, and upon mixing it is ready for use. The tubes containing 2, 3, 4, and 5 ml. of standard solution are usually most convenient.

From the above data the concentration of nitric oxide in the gas can be calculated. In most cases, the probable error of this comparison can be held under 3 per cent without great difficulty.

Calculations

Assume the following test data: Volume of mixed gas reduced to 60° F. and 30 inches of mercury = 0.444 cu. foot. Color developed during test = 4.2 ml. of standard solution.

Then $\frac{4.2 \times 0.0388}{0.444} = 0.37$ p. p. m. of nitric oxide in coke-oven gas (observed value).

Where gas volumes are corrected to 0° C. and 760 mm. of mercury, use factor 0.0362 instead of 0.0388.

Discussion of Method

Most analytical methods are empirical. This method is markedly so. Any change in apparatus or procedure is likely to produce a change in results, and even the shape of the bottle is important. The indicator is ultrasensitive. Ultrasensitive technic must, therefore, be employed.

This method is designed for use with coke-oven gas. It is believed that it cannot be used for water gas analysis without some change.

Griess reagent apparently cannot be used interchangeably with *m*-phenylenediamine. While the former is certainly more delicate, tests by various analysts in the author's organization indicate that it is less active at normal room temperatures.

The *m*-phenylenediamine reagent should be shielded from strong light which causes a darkening effect, giving falsely high results. It may be handled with impunity indoors or out of direct sunlight. Out-of-doors, it is recommended that the container be covered with a cloth or otherwise shielded. Any damage due to light is usually evident to the observant eye. This may have been the source of off-colors frequently reported in the early days of this work.

Because of a purging lag which is more or less inherent in this type of setup, the apparatus cannot be used on gas of high nitric oxide content and then after a short purge be safely used on gas of a low nitric oxide content. The apparatus must first be cleaned. This consists in rinsing out and replacing all chemicals and in rinsing out the delay bottle with water and with acetone, and in blowing with air or other nitric oxide-free gas to remove the acetone thoroughly. Small amounts of acetone seriously interfere with color formation in the *m*-phenylenediamine. This cleaning process requires about 10 minutes. It is recommended that this cleaning be done daily.

With this method of procedure, the observed value for nitric oxide was found to be almost exactly half the true value. Fairly authentic tests run at three different coke plants indicated that this factor is common to all of them.

Flowmeters have been used by some workers for measuring the gas as well as the oxygen. The writer has observed instances where the flowmeter orifice has caused a deposit of

gum from the gas. A flowmeter is, therefore, not recommended for this purpose.

The small gas governor with spring-type adjustment affords a convenient, though not entirely necessary, means of keeping a constant pressure at the inlet of the apparatus, thus aiding gas flow adjustment. It would, of course, be open to the same objection as the flowmeter. It is possible that both might be placed after the apparatus.

The foregoing method applies only to gas carrying small amounts of ammonia and hydrogen sulfide, as will be realized upon considering the quantities of acid and alkali employed. If it is desired to use the method on unpurified gas, it is suggested that the gas be first passed through a single bubbling bottle each of the acid and alkali solutions. The bulk of the solutions should be no greater than necessary and the bottles should be as nearly full as convenient. The principal purpose of the potassium hydroxide appears to be the removal of active sulfur compounds and the control of humidity.

Apparatus of this type determines neither suspended gum particles nor nitrogen peroxide. It is obvious that either of these substances existing in the gas sample in a form that can be absorbed will be removed before the gas reaches the delay bottle. Ordinarily, though not always, these substances are present in negligible amounts only.

Some of the nitric oxide in the gas goes through the apparatus untouched, as shown by the fact that when two of these analytical setups are run in series, a small amount of color will be formed in the second. However, this seems to be a fairly constant percentage of the whole and is taken care of by the factor of 2 previously mentioned. This factor is an over-all correction figure derived from nitric oxide found divided by nitric oxide added.

It is customary to report observed values rather than actual values for nitric oxide, which in this case are half the actual. It is therefore important to indicate whether figures used are observed or actual.

The writer prefers to report the nitric oxide in parts per million (by volume). It is a universally understood unit, in plant work it is usually a simple decimal rather than a mixed number, and it has the advantage of being a scientifically correct and accepted nomenclature.

The 3-minute contact period was chosen as the result of a series of experiments which showed that the percentage of nitric oxide recovered increased very sharply up to a period of about 2 or 2.5 minutes' delay time and then gradually dropped off. A 3-minute period, therefore, gave a point of approximately maximum recovery, and at the same time allowed for small rate variations on either side of the theoretical without causing large errors in the results obtained. Figure 3 shows the result of this series of tests.

The oxygen required in the delay bottle is not a critical amount. The percentage recovery of nitric oxide was about the same with a concentration of 0.5 per cent and with one of 50 per cent.

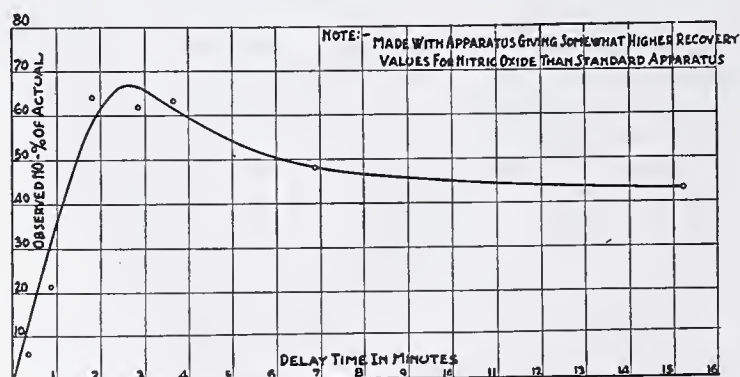


FIGURE 3. RELATION OF DELAY TIME TO OBSERVED NITRIC OXIDE

TABLE I. EFFECT OF TEMPERATURE UPON NITRIC OXIDE ANALYSIS

Expt. No.	Observed NO, Per Cent of Actual	Actual NO in Gas P. p. m.	Temperature ° C.
69 T1	58	0.11	48
T2	55	0.11	48
70 T1	56	0.11	50
71 T1	52	0.12	25
T2	58	0.13	48
72 T1	53	0.16	23
76 T1	52	1.12	23
77 T1	60	1.07	44
T2	47	1.08	48
T3	53	1.06	50
T4	48	1.10	50
T5	52	1.07	49
T6	47	1.08	49

TABLE II. ACCURACIES ATTAINED

Expt. No.	Added NO (Actual) P. p. m.	Observed NO, Per Cent of Actual	Remarks
R-367-30	0.000	0.000	No color during 7-hr. run
E-63	0.057	60	
E-64	0.11	52	
E-64	0.12	51	
E-71	0.12	52	
E-72	0.16	53	
E-94	0.89	55	
E-94	0.91	54	
E-94	0.88	56	
E-95	0.90	57	Per cent of oxygen = 5.0
E-95	0.94	58	Per cent of oxygen = 9.2
E-93	0.93	52	
E-93	0.95	52	
E-98	1.02	57	
E-S125	1.51	51	Gas from plant II
E-S125	1.51	53	
E-96	1.91	53	
E-96	1.89	56	
E-96	1.84	53	

The delay bottle should be dry at all times. The gas in the bottle should be substantially below its saturation point. Very erratic results can be obtained by ignoring this point.

A sample line should never be heated during the time the nitric oxide apparatus is on the line. It is suggested that the sample lines be oversize and as short as possible and arranged so that they may be blown out with steam and cooled and purged before the nitric oxide apparatus is put on the line. Very high results can be obtained by heating a fouled sample line.

The apparatus should be used in a room having a reasonably even temperature. It was not observed by the writer that ordinary changes in temperature had any very drastic effect on the results. It is, however, possible to produce incorrectly high results by effecting a sharp and unusual rise in temperature, especially if the apparatus is unclean or has been operating for a long period. It is also true that at greatly reduced temperatures the *m*-phenylenediamine reagent appears to lose some of its activity. It is therefore recommended that when working below 18° C. (65° F.) low temperature be compensated for. It is believed that this condition will be encountered so seldom that it is unwise to burden the regular setup with a thermostatically controlled container.

A great deal of discussion has centered around the desirability of putting the setup under thermostatically controlled conditions. To do this properly would be expensive and would result in a cumbersome setup. The writer does not believe it is necessary. With a clean setup, good results can be obtained at advanced temperatures as Table I will indicate. During this test series, it appeared that the heated apparatus tended to give more erratic results than the unheated. In view of the conditions involved, this is not especially surprising.

Table II gives a general idea of the accuracies attained.

In E-95, the per cent of oxygen was nearly doubled without apparent effect upon the recovery of nitric oxide.

At a certain large coke plant, not included in the previous discussion, the gas was being experimentally treated for nitric oxide removal on a full plant scale. It was known that the method employed gave uniform and nearly complete removal of nitric oxide under optimum conditions. A series of routine efficiency tests, run daily upon this treater by this method for a period of about one week, showed removal efficiencies of 94, 93, 97, 93, 96, and 95 per cent.

Summary

An improved method for determination of the traces of nitric oxide usually found in coke-oven gas and the procedure used to check this analytical method, by adding extremely small measured amounts of nitric oxide to nitric oxide-free coke-oven gas, have been described.

By use of this analytical method approximately one-half of the nitric oxide actually in the gas is recovered and determined by a colorimetric method. Therefore, a factor of 2 is applied to the observed value to give the actual content of nitric oxide.

The effects of variables such as delay time, added oxygen, temperature, etc., have been described.

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Titration of Silver with Potassium Iodide
Ceric Ammonium Sulfate and Starch as Indicators

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ACCORDING to Shapiro (4), in the determination of chlorides by the Volhard method, excess silver may be titrated in a nitric acid solution with potassium iodide. The end point is detected in the presence of starch when the nitric acid oxidizes the iodide to iodine. Schneider (3) suggests the use of palladium nitrate as an indicator, noting the end point by the formation of a red-brown precipitate of palladous iodide. Fleury and Courtois (1) and Josien (2) recommend the use of starch-iodine-potassium iodide solution, in which

the silver solution must be added to the starch-iodine-potassium iodide solution.

The method described by the authors consists of the titration of silver with potassium iodide in the presence of ceric ions and starch. Oxidation of the iodide ion to iodine by the ceric ion is not permanent until the end point is reached. During the course of the titration a blue color appears, but is immediately discharged upon stirring. The method gave good results in the presence of ferric and cupric ions.

Analytical Procedure

Ten or 20 cc. of a 0.1 N silver nitrate solution were transferred to a 200-cc. beaker. To this were added water and a sufficient amount of sulfuric acid to give a volume of approximately 110 cc. (concentration of acid may vary from 0.2 N to 3 N), and then 3 cc. of 0.5 per cent starch solution and 0.1 cc. of an approximately 0.1 N ceric ammonium sulfate solution. It is important to add the sulfuric acid before the ceric ammonium sulfate. The silver was titrated with 0.1 N potassium iodide solution. The end point was sharp and easily detected when the last drop of potassium iodide gave a permanent blue-green color to the solution. Blank titrations were made under the same conditions omitting the silver nitrate. The blank consumed 0.1 cc. of the potassium iodide solution before a permanent color was obtained.

Summary

A method is described for the titration of silver with potassium iodide, using ceric ammonium sulfate and starch as internal indicators. The acid concentration may vary in the titration from 0.2 N to 3 N without appreciable error. The titration can be made in the presence of cupric and ferric ions.

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TABLE I. TITRATION OF SILVER

ACIDITY N	0.1 N KI Cc.	0.1 N KI with Blank Correction Cc.
10 cc. of 0.1 N AgNO ₃ solution in a volume of 110 cc.		
0.2	10.14	10.04
0.5	10.14	10.04
1.0	10.16	10.06
2.0	10.18	10.08
3.0	10.16	10.06
20 cc. of 0.1 N AgNO ₃ solution in a volume of 110 cc.		
1.0	20.08	19.98
2.0	20.11	20.01
3.0	20.12	20.02

TABLE II. TITRATION OF SILVER NITRATE

(10 cc. of 0.1 N AgNO₃ solution in the presence of cupric and ferric ions. Volume approximately 110 cc., acidity approximately 0.5 N)

0.1 N CuSO ₄ ·5H ₂ O and FeNH ₄ (SO ₄) ₂ ·12H ₂ O Cc.	0.1 N KI Cc.	0.1 N KI with Blank Correction Cc.
CuSO ₄ ·5H ₂ O		
10	10.10	10.00
30	10.13	10.03
50	10.14	10.04
FeNH ₄ (SO ₄) ₂ ·12H ₂ O		
10	10.15	10.05
30	10.12	10.02
50	10.17	10.07
{ 50 FeNH ₄ (SO ₄) ₂ ·12H ₂ O 50 CuSO ₄ ·5H ₂ O	10.12	10.02

Turbidity in Sugar Products

IV. Preparation of Raw Sugar Solutions for Determination of Color and Turbidity

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IT HAS been shown previously (5) that the concentration of the turbidity present in a solution of a raw sugar may be measured, on the basis of transmittancy and Tyndall beam intensity, in terms of the specific absorptive index of an equivalent turbidity caused by particles of standard properties, and that the deviation in the properties of the particles actually present from those of the standard may be characterized by the "quality index" and by the dispersion quotient.

The question of determining the concentration of coloring matter or, in other words, of correcting the specific absorptive index of filtered solutions for the residual turbidity present was left open, but it was postulated that coloring matter shall be defined as that portion of the dispersed material which gives a Tyndall beam of zero intensity under the experimental conditions used. This correction for residual turbidity has been further investigated, and an attempt has been made to find a filtering material which would leave in the filtrate only the total coloring matter, as defined above. This opened up again the much discussed problem of the removal of turbidity and coloring matter by filtering agents, which was previously studied by Peters and Phelps (3), Brewster and Phelps (2), and by Balch (1).

Peters and Phelps did not give the detailed results of their investigation, but promised a later publication which has not yet appeared. In the original article they reported only comparisons between the specific absorptive index of solutions of about 52 to 53 Brix, filtered through specially prepared asbestos, and that of solutions of about 1 to 7 Brix, mixed with kieselguhr and filtered through paper. They found that the latter were always very turbid when examined in the dark room, whereas the highly concentrated asbestos filtrates showed only a faint Tyndall cone. The $-\log t$'s of the kieselguhr filtrates, at various wave lengths throughout the visible spectrum, were irregularly higher or lower than the corresponding values for the asbestos filtrates, and these discrepancies were ascribed to selective adsorption by the kieselguhr, to the presence of finely divided kieselguhr in the dilute filtrates, and to differences in the colloid equilibrium of dilute and concentrated solutions. Peters and Phelps concluded that a correct measure of the coloring matter could be obtained only by their method of filtering concentrated solutions through asbestos.

Brewster and Phelps rejected purified standard Filter-Cel even for the filtration of concentrated solutions, on the ground that it removes actual coloring matter, because decolorization is more extensive when more Filter-Cel is used.

Balch, on the other hand, concluded from his experiments that Filter-Cel does not adsorb coloring matter, or at most very little, and that it is permissible to use this agent for colorimetric analysis, or for preparing solutions to be used as standards of comparison for turbidity measurements.

In view of these divergent opinions, the entire subject of preparing sugar solutions for colorimetric analysis has been reinvestigated. The factors studied were concentration of the sugar solution, cell thickness, colloid equilibrium, and the effect of various filtering agents on the transmittancy and Tyndall beam intensity of the resulting solutions.

Concentration of Sugar Solution

The necessity of using, for colorimetric analysis, as high a concentration of dry substance as is compatible with reasonably rapid filtration has been well shown by Brewster and Phelps, who advocate solutions of at least 60 Brix, which is

somewhat higher than the minimum figure given by Peters and Phelps. The proper choice of concentration is important not only for solutions to be filtered, but also in preparing raw sugar solutions for turbidity determinations. A 65 Brix solution of a raw sugar, when strained through a 250-mesh bronze screen to remove coarse suspended matter, gave consistently higher $-\log t$ values at three selected wave lengths in the blue, green, and red, than a 60 Brix solution, strained the same way; the dispersion quotients for red to green were lower, while those for blue to green changed irregularly. The Tyndall beam intensity and its dispersion quotients were also affected, changes in either direction being observed. This makes it necessary to standardize conditions for both color and turbidity measurements, and a concentration of 60 Brix has been chosen by the writers, because this permits a fairly rapid filtration even for poorly filtering sugars. It is also advisable to remove coarse suspended matter by centrifuging under standard conditions rather than by straining through a screen, because the coarse suspended matter forms a filter bed which is liable to retain varying quantities of the more highly dispersed particles whose quantity is to be measured.

Cell Thickness

If turbidity measurements are to be made according to Balch's or the writers' method, it is necessary to keep not only the concentration of dry substance but also the cell thickness constant. The constants in the formulas given in the preceding article of this series (5) apply only to the cell thickness used, 2.46 mm. No attempt has been made so far to derive formulas for varying thickness, but the fact has been well established that for turbid colored solutions there is no simple relationship between depth of layer and $-\log t$ or Tyndall beam intensity. When only filtered solutions are to be used for color determination, the depth of layer may of course be varied as desired.

Colloid Equilibrium

Possible changes in the colloid system in the solutions, between the time of preparation and the time of measurement, must be given proper consideration. The writers found irregular changes in the $-\log t$ as well as the Tyndall beam intensity, when 60 to 65 Brix solutions were allowed to stand in the refrigerator for 2 or more days. The changes were not very pronounced, but it has been found advisable to make the optical measurements as soon as colloid equilibrium is established, which is about 2 hours after the solutions have been prepared.

Some very interesting observations have been made regarding the effect which a change in water or sucrose concentration has on the colloid equilibrium. If an aqueous solution of caramel is carefully filtered through purified Filter-Cel, and then mixed with an equal volume of a 60 Brix raw sugar solution, which has likewise been filtered through Filter-Cel, the $-\log t$ of the mixture is higher than when the unfiltered solutions of caramel and raw sugar are first mixed and then filtered with Filter-Cel. The same is true to even a greater extent when pure sucrose or water is substituted for the raw sugar, as may be seen from Table I.

The dilution with water produces partial flocculation of the caramel particles, and the larger particles are removed by subsequent filtration. It is difficult to understand, however, why mixing the caramel solution with a 60 Brix sucrose solution, which amounts to addition of a protective colloid, should have the same effect, and of greater magnitude, as dilution with water. The probable explanation is that there is an interaction between the sucrose molecules and the caramel particles, with the formation of larger aggregates, which are then removed by filtration with Filter-Cel. If this explanation is correct, then it further follows that in a raw sugar solution similar aggregates between the sucrose and the coloring matter are already preformed, and less sucrose is available to combine with the caramel. This would explain why in the case of the raw sugar the difference in the $-\log t$'s was so much smaller than in that of sucrose or water. The same effects were noted when powdered glass (see below) was used as the filter medium, instead of Filter-Cel. After a mixture of caramel and sugar sirup had once been filtered through Filter-Cel, a second filtration through powdered glass had no further effect.

TABLE I. EFFECT OF CHANGE IN WATER OR SUCROSE CONCENTRATION

	Solutions Filtered Separately, Then Mixed, $-\log t$	Solutions Mixed and Mixture Filtered, $-\log t$
Caramel plus raw sugar solution	0.516	0.504
Caramel plus sucrose solution	0.371	0.258
Caramel plus water	0.374	0.275

In experiments similar to those described above, the aqueous caramel solution was replaced by a 60 Brix solution of a dark raw sugar. When this solution was treated with a 60 Brix solution of another, light colored sugar, the same $-\log t$ at 560 $m\mu$ was obtained, no matter whether the solutions were first filtered separately and then mixed, or first mixed and then filtered.

The results of the tests with caramel solution and with sugar sirups confirm the conclusion reached by Peters and Phelps that dark colored sugar products like molasses must not be diluted with water previous to color determination, but with a white sugar sirup.

As far as the $-\log t$ is concerned, the molasses could first be filtered separately, if that were physically possible, and then mixed with the filtered white sugar sirup, or else it could first be mixed with the white sugar sirup and the mixture then filtered, as is actually done in practice. There is, however, a slight difference in the colloid equilibrium of the mixtures prepared by the two methods, as is evidenced by Tyndall beam measurements in the following experiment:

A 60 Brix raw sugar solution was filtered through purified Filter-Cel, and then mixed with an equal volume of 60 Brix white sugar sirup which had also been carefully filtered (mixture A). Another, unfiltered portion of the raw sugar sirup was first mixed with an equal volume of filtered white sugar sirup, and the mixture filtered through Filter-Cel (mixture B). Tyndall beam readings were then taken with the Pulfrich photometer in cells of the same thickness, and the values given in Table II were obtained, in per cent of the intensity of the standard block, immediately after preparation, and again after equilibrium was established.

TABLE II. EFFECT OF METHODS OF PREPARATION

Wave Length	Immediately after Preparation		At Equilibrium	
	A	B	A	B
529 $m\mu$	29.0	42.0	34.7	18.9
621 $m\mu$	138.5	265.6	177.9	87.0

After equilibrium had been established, method B, which is the one usually followed, gave a solution better fitted for colorimetric analysis.

Filtering Materials

In the new investigation on filtering materials adapted for colorimetric and turbidimetric analysis the following substances were used: asbestos, Filter-Cel, filter paper, Jena fritted-glass funnels, the Seitz filter, ground glass, and silica gel.

The asbestos, XXX grade, was purified and used for the preparation of the samples as described by Peters and Phelps (3).

The Filter-Cel was the analytical filter aid marketed by the Johns-Manville Corporation. To purify it further, 75 grams were boiled with a mixture of 100 cc. of concentrated hydrochloric acid and 900 cc. of distilled water, then filtered hot and thoroughly washed with hot water. This treatment was repeated three times, and finally the material was dried and ignited in a muffle furnace.

Jena fritted-glass funnels of various porosities were employed, mostly as a backing for asbestos, instead of Gooch crucibles, but the No. 4 type was also used directly. The filter paper was S. & S. No. 575.

The Seitz filter was the small laboratory model pressure outfit. The disks furnished by the manufacturers were used, and the filtrations were carried out with the aid of compressed nitrogen, at pressures up to 5.62 kg. per sq. cm. (80 pounds per sq. inch), depending on the filterability of the solution.

The Jena ground glass was the grade G 20, No. 4, having an average particle diameter of 5 to 10 $m\mu$. (The writers thank Murray Yawitz of the Fish-Schurman Corporation for his generous cooperation in supplying the ground glass and in investigating the Jena fritted-glass funnels adaptable for their work.)

The silica gel, kindly furnished by the Silica Gel Corporation, was the air-floated, medicinal type. It was found to be slightly acid, and was therefore boiled out twice with distilled water, filtered after each boiling, washed, dried, and ignited.

The Seitz apparatus was found to be an efficient ultra-filter. It easily reduces the turbidity in raw sugar solutions to that found in distilled water, but visibly decolorizes them. As an example, the figures in Table III are given for $-\log t$ and Tyndall beam intensity, R , of a 60 Brix raw sugar solution, treated as specified.

TABLE III. EFFICIENCY OF SEITZ FILTER

	$-\log t$		R	
	529 $m\mu$	621 $m\mu$	529 $m\mu$	621 $m\mu$
Centrifuged	2.814	2.649	1157	4098
6 times through asbestos	2.424	1.257	354	1376
Same, then through Seitz filter	2.010	0.908	98	297
7 times through Seitz filter	1.463	0.656	35	90

Since the Seitz filter evidently removes a large proportion of the coloring matter, and since it requires pressure filtration, its use was not further investigated.

An example of the effect of some of the other filtering materials, as compared to asbestos, is shown in Table IV.

TABLE IV. EFFECT OF FILTERING MATERIALS

	$-\log t$, 560 $m\mu$	$-\log t$, 620 $m\mu$
Asbestos	1.187	0.672
Filter-Cel	1.062	0.599
Jena funnel No. 4	1.322	0.781
Ground glass, on Jena funnel No. 4	1.122	0.616
Filter paper	1.378	0.818

Ground glass gave a lighter filtrate than asbestos filtration, but was not as efficient as Filter-Cel. The Jena funnel No. 4 produced a much darker filtrate, and the filter paper a still darker one. In other experiments it was found that ground glass and Filter-Cel combined give practically the same result as Filter-Cel alone. When ground glass was used in connection with the Seitz filter, it reduced the Tyndall beam intensity to about one-half that obtained with the Seitz filter alone, but the $-\log t$ was not measurably affected. None of these materials, except asbestos and Filter-Cel, offered sufficient advantages to warrant further study.

Comparative Tests of Asbestos, Filter-Cel, and Silica Gel

Silica gel, however, gave such encouraging results in preliminary trials that its effects were more thoroughly investigated, in comparison with asbestos and Filter-Cel, the filtering agents already widely used.

MECHANISM OF REMOVAL OF TURBIDITY. The first problem taken up was the mechanism of the removal of turbidity from turbid solutions, in order to ascertain whether this removal is due to mechanical filtration or to adsorption, and whether there is a distinct demarcation between turbidity and coloring matter.

Balch had previously found, contrary to Brewster and Phelps, that when a raw sugar solution was clarified with Filter-Cel, the same $-\log t$ was obtained, no matter whether 1, 2, or 3 grams of the filtering agent were added.

In repeating and extending the experiments of these previous investigators, a 60 Brix solution of a raw sugar was prepared, and 50-ml. portions were filtered with from 1 to 5 grams of asbestos, Filter-Cel, and silica gel. The asbestos was used in the form of a pad on a No. 2 Jena fritted-glass funnel, and was allowed to pack itself under the pressure of a water-jet filter pump. The Filter-Cel and the silica gel were mixed with the solution to be filtered, and the mixture was filtered through a double layer of S. & S. filter paper, No. 589, blue ribbon, on a 7-cm. Büchner funnel. The results, in terms of $-\log t$, at wave length 560, of the filtrates, are shown in Table V.

TABLE V. EFFECT OF QUANTITY OF FILTER MEDIUM

Filter medium, grams	1	2	3	4	5
Asbestos	2.032	1.616	1.711	1.784	1.711
Filter-Cel	1.592	1.470	1.476	1.457	1.461
Silica gel	1.456	1.435	1.429	1.436	1.422

One gram of asbestos allowed a large portion of the turbid material to pass through. The figures obtained with the larger amounts of asbestos are very irregular, and this is probably due more to differences in the packing of the asbestos in the pads than to any other cause, as will be shown below. The average of the results with 2 and 4 grams agrees closely with the figures obtained by using 3 or 5 grams.

In earlier unpublished work carried out by Peters and one of the writers, working side by side, portions of the same raw sugar solution, prefiltered after shaking with asbestos, were passed six times through the final pads. Each worker used his own asbestos, Powminco XX and XXX, respectively, pretreated as described by Peters and Phelps. It was at once noticed that the pad prepared by Peters gave a much more rapid filtration than the other, and the filtrate was visibly darker in transmitted light. The $-\log t$'s, found with the spectrophotometer from readings made by both observers, are given in Table VI.

TABLE VI. TESTS WITH ASBESTOS

Wave Length, m μ	Peters		Zerban	
	1.5 Grams of XXX — log t	Asbestos Q-ratio	2 Grams of XX — log t	Asbestos Q-ratio
480	2.530	1.99	1.903	2.15
560	1.272	1.00	0.885	1.00
660	0.594	0.47	0.340	0.38

The fact that XX grade asbestos was used as the raw material for the pad in one case, and XXX grade in the other, may have some bearing on the results, but it should be noted that Peters and Phelps and also Brewster and Phelps recommend either grade for colorimetric analysis. The principal reason for the discrepancies must be the packing of the asbestos, made manifest by the speed of filtration. The slow pad evidently had a sort of ultrafiltration effect, similar to that noticed with the Seitz filter. The Q-ratios show that the particular coloring matter taken out by this pad was different

in character from that remaining behind in the filtrate. The important conclusion to be drawn from these experiments is that asbestos removes coloring matter selectively, and does not differ from Filter-Cel in this respect. Workers in the same or different laboratories will obtain different results on the same sugar if their asbestos pads are of different permeability, a property which is very difficult to standardize.

The values obtained with Filter-Cel, Table V, are more uniform than those with asbestos. Again, 1 gram removed less dispersed material than the larger quantities, but the maximum difference between the $-\log t$ figures for 2 to 5 grams is only 1.3 per cent, which is well within the limits of error. All the results are decidedly lower than the corresponding ones for asbestos filtration.

In the case of another raw sugar, 200 grams of 60 Brix solution were filtered with 6 grams (5 per cent of dry substance) of Filter-Cel, and the $-\log t$ was found to be 0.619. When the filtrate was again treated with 6 grams of Filter-Cel, the $-\log t$ was 0.628, the same within the limits of error. While these results confirm similar observations made by Balch, still other sugars (50 ml. of 60 Brix solution) were found to behave differently, as may be seen from Table VII.

TABLE VII. TESTS WITH FILTER-CEL

Grams of Filter-Cel	Sugar 3					
	0.000	0.125	0.375	0.750	1.375	2.500
— log t at 560 m μ	0.471	0.431	0.419	0.417	0.391	0.374

Grams of Filter-Cel	Sugar 4				
	1	2	3	4	5
— log t at 560 m μ	1.248	1.225	1.204	1.180	1.163

In both cases there is a gradual falling off in the $-\log t$ with increasing quantities of Filter-Cel. It is evident that for these two sugars more Filter-Cel than the maximum quantity tested would have to be used, in order to reach the limiting effect. This was also recognized by Balch, who states that the quantity of Filter-Cel to be used depends on the quantity and character of the suspended material present.

The same observation applies also to silica gel. Sugar 1, Table V, has the same $-\log t$, within a maximum error of 1 per cent, whether 2, 3, 4, or 5 grams of the filtering agent are used, and this effect was almost reached even with 1 gram. But other sugars (50 ml. of 60 Brix solution) gave the figures in Table VIII.

TABLE VIII. TESTS WITH SILICA GEL

Grams of silica gel	1	3	5	10
— log t, 560 m μ , sugar 5	..	0.413	0.356	0.357
— log t, 560 m μ , sugar 6	1.064	0.983	0.982	..

Sugar 5 required 5 grams for the maximum effect, sugar 6 only 3 grams. With sugar 1 (Table V) silica gel gave a lighter colored filtrate than the same quantity of Filter-Cel, and a much lighter one than asbestos.

The selective effect of the three filtering materials was investigated with four other raw sugars, by making transmittancy readings at three wave lengths with the Pulfrich photometer. The first two sugars were dark in color, but the solutions were not very turbid; the third was light in color, with medium turbidity; and the fourth was also light colored but highly turbid. The asbestos was used according to the Peters and Phelps technic, 50 ml. solution of 60 Brix being filtered six times through a pad of 3 grams of asbestos in a No. 2 Jena fritted-glass crucible. Filter-Cel and silica gel were used at the rate of 3 grams per 50 ml. of solution, and the mixtures filtered through filter paper, S. & S. No. 589, blue ribbon.

The $-\log t$'s at the three wave lengths, and the R-ratios (dispersion quotients) based on wave length 529 m μ are shown in Table IX.

TABLE IX. SELECTIVE EFFECT OF FILTERING MATERIALS

Sugar No.	Wave Length, $m\mu$	Asbestos		Filter-Cel		Silica Gel	
		$-\log t$	R-ratio	$-\log t$	R-ratio	$-\log t$	R-ratio
7	449	5.915	2.01	5.317	2.00	5.201	2.02
	529	2.949	1.00	2.655	1.00	2.574	1.00
	621	1.301	0.44	1.118	0.42	1.092	0.42
8	449	3.679	1.77	3.258	1.89	2.795	1.91
	529	2.079	1.00	1.722	1.00	1.467	1.00
	621	1.211	0.58	0.986	0.57	0.841	0.57
9	449	0.588	2.09	0.525	2.20	0.511	2.30
	529	0.281	1.00	0.239	1.00	0.222	1.00
	621	0.135	0.48	0.115	0.48	0.107	0.48
10	449	0.595	1.60	0.316	1.77	0.242	1.80
	529	0.372	1.00	0.179	1.00	0.135	1.00
	621	0.249	0.67	0.120	0.67	0.078	0.58

Asbestos filtration again gave the highest $-\log t$ values at all wave lengths, followed by Filter-Cel and then by silica gel. The differences between asbestos on the one hand and Filter-Cel or silica gel on the other are most pronounced in sugar 10, of low color and high turbidity. In sugar 7, the R-ratios are about the same for the three filtering agents, and there is practically no selective action, but in the other three the ratios increase at the blue end, from asbestos through Filter-Cel to silica gel. At the red end the ratios are not affected to any great extent, except in sugar 10, where the silica gel gave a much lower ratio than either asbestos or Filter-Cel.

The question arose whether the selective action of the three filtering materials is due to adsorption or to a purely mechanical filtration effect. It is well known that when sugar coloring matter is removed by means of activated carbons, the mechanism is that of true adsorption, in accordance with Freundlich's equation:

$$\frac{x}{m} = KC^{1/n}$$

where C = concentration of color left in solution

x = concentration of color removed by adsorbent

m = weight of adsorbent

When the figures in Tables V, VII, and VIII are analyzed from this standpoint it is seen that the removal of the dispersed material by any of the three filtering agents is entirely irregular. Although Tables VII and VIII indicate a progressive decrease in the $-\log t$'s, the quantity of dispersed material taken out per unit of filtering agent bears no constant relation to the quantity of dispersed material left in the solution.

While these observations point to a purely mechanical effect of the filtering agents, it was nevertheless desirable to substantiate this finding by a more direct proof. The writers have previously shown that this proof may be furnished by a technic originally employed by Balch. The material to be tested is added in one case to a white sugar sirup, and in the other to a colored sugar sirup. Then the turbid white sirup is read against the clear white sirup in a spectrophotometer, and the turbid colored sirup is read against the clear colored sirup. If no adsorption occurs, then the two transmittancy readings must be the same. Balch showed that the bentonite used by him follows this rule. In similar experiments the writers were able to show (4) that Filter-Cel does not adsorb coloring matter from caramel solution, but that a sample of bentonite different from that used by Balch did adsorb coloring matter. It was decided to repeat these experiments, and to extend them to asbestos and silica gel as filtering agents.

Five grams of asbestos, Filter-Cel, and silica gel were each ground in a mortar with 50 ml. of a 60 Brix white sugar sirup. The suspension was poured into a flask and allowed to settle in the refrigerator for 4 days. It was then decanted into a fresh portion of white sirup, and the mixture was shaken and again placed for 4 days in the refrigerator. The suspension thus obtained was decanted into a clean, dry flask, and was gently shaken immediately before being used in the experiments.

It was necessary to employ a raw sugar to furnish the colored sirup, because results with caramel or any other coloring matter could not be accepted as proof for the behavior of sugar coloring matter. The turbidity naturally present in the sugar had to be removed as far as possible by prefiltration. Both the raw sugar and the white sugar sirup, of 60 Brix concentration, were therefore prefiltered with one of the three filtering agents mentioned above, and the turbid sirups were prepared with either of the others, or each of the three.

In the first series of tests Filter-Cel was used for the preparation of both sirups, by the same procedure as previously described. Two equal portions of the filtered raw sugar sirup and two of the filtered white sirup were measured from a microburet. One portion each of colored and of white sirup was then made up to a definite volume with asbestos suspension, to produce the turbid sirups, while the remaining two were diluted to the same volume with filtered white sirup, to produce the clear sirups, one colored, the other white. The turbid colored sirup was read in the spectrophotometer, at wave lengths 529 and 621 $m\mu$, against the clear colored sirup, and the turbid white sirup against the clear white sirup. Exactly the same experiments were made with silica gel suspension instead of asbestos suspension.

In the second series of tests the prefiltration was carried out with silica gel; asbestos, Filter-Cel, and silica gel were used to produce the turbidity in the filtered sirups. In the third series the sirups were prefiltered with asbestos, and suspensions of Filter-Cel or silica gel were added to the filtered sirups. The results of the transmittancy measurements are shown in Table X.

TABLE X. TRANSMITTANCIES OF TURBID vs. CLEAR SIRUPS

Wave Length, $m\mu$	Asbestos		Filter-Cel		Silica Gel	
	Colored sirups	White sirups	Colored sirups	White sirups	Colored sirups	White sirups
A. Filter-Cel used for prefiltration						
529	40.4	40.5	42.8	43.2
621	45.9	46.9	49.9	51.3
B. Silica gel used for prefiltration						
529	64.2	64.3	47.4	47.1	56.1	57.2
621	69.9	70.9	55.7	55.8	65.2	65.5
C. Asbestos used for prefiltration						
529	..	27.1	26.5	..	62.9	72.1
621	..	33.4	33.1	..	68.6	77.0
					(Other concn.)	
529	29.7	40.0
621	37.3	48.0
Very thorough prefiltration with asbestos						
529	41.4	45.4
621	50.7	54.4

When either asbestos or Filter-Cel is used to produce turbidity, the transmittancies are the same within the limits of error, showing that neither of these filtering agents adsorbs coloring matter. The silica gel behaves differently, however. In the raw sugar sirup prefiltered with asbestos, the silica gel apparently produces adsorption, but in those prefiltered with Filter-Cel or silica gel it does not, or only to a very limited extent. The effect is also greatly reduced by thorough prefiltration with asbestos. These facts indicate that silica gel adsorbs only particles of a certain size, not removed by prefiltration, but has no effect beyond that limit. Filtration with silica gel is therefore not essentially different from filtration with asbestos or Filter-Cel, but is more effective than either.

Having established the mechanism of the removal of dispersed matter by the three filtering agents, all three were used on another series of twelve raw sugars of varying characteristics, transmittancy and Tyndall beam measurements being made on the unfiltered and the filtered solutions by the procedure described in the preceding paper (5).

All filtrations were made by suction with a water-jet pump. Large filtering tubes were used, in the top of which the Büchner funnel or Gooch crucible was inserted by means of a rubber stopper. The filtering tube (Figure 1) had a side arm near the top and a glass stopcock at the lower end. The side arm of the filter tube was connected by means of a Y-tube with the side arm of the filter flask and then with the suction pump. This arrangement made it possible to discard the first 25 ml. of filtrate and to collect the very clear portion of the filtrate without breaking the vacuum, which would disturb the filter bed already formed.

The method described by Peters and Phelps for the preparation of the asbestos pads, by suction only, had always given rather poor filtrates when examined in the dark room. For this reason the asbestos layer in the present series of experi-

ments was first moistened with the sugar solution to be filtered, and then packed down tightly, while under suction, by means of a flattened glass rod. The filtrates thus obtained were visibly better than those prepared by the old method. In all other respects the standard procedure of preliminary shaking with asbestos and filtration, followed by six successive filtrations through the optical pad, was followed.

In the case of Filter-Cel, 3 grams of this material were added to 50 ml. of the 60 Brix sugar solution, and the mixture was thoroughly shaken and filtered by suction through a double layer of S. & S. filter paper No. 589, blue ribbon, in a 7-cm. Büchner funnel. About 25 to 30 cc. of the filtrate were allowed to pass through before a sample was collected

TABLE XI. MEASUREMENTS ON RAW SUGARS

No.	$-\log T$	R	N	C	$-\log T_u$ $-\log T_f$	$-\log T_f$ C	N_u $-\log T_u - C$	No.	$-\log T$	R	N	C	$-\log T_u$ $-\log T_f$	$-\log T_f$ C	N_u $-\log T_u - C$
A. Blue Filter															
11	U 1.199	228.5	0.750	0.449	FA	0.275	37.8	0.013	0.262	0.232	1.050	0.808
	FA 0.377	10.6	0.025	0.352	0.822	1.071	0.885	FC	0.251	22.2	0.008	0.243	0.256	1.033	0.750
	FC 0.372	6.9	0.016	0.356	0.827	1.045	0.890	FS	0.226	21.7	0.006	0.220	0.281	1.027	0.690
	FS 0.324	5.4	0.011	0.313	0.875	1.035	0.847	18	U 0.665	782.1	0.335	0.330
12	U 0.566	123.7	0.252	0.314	FA	0.249	62.3	0.020	0.229	0.416	1.087	0.768
	FA 0.316	13.6	0.026	0.290	0.250	1.090	0.913	FC	0.219	29.8	0.009	0.210	0.446	1.043	0.736
	FC 0.322	8.6	0.017	0.305	0.244	1.056	0.966	FS	0.172	29.9	0.008	0.164	0.493	1.049	0.669
	FS 0.261	9.9	0.016	0.245	0.305	1.065	0.785	19	U 1.001	990.0	0.576	0.425
13	U 1.303	188.6	0.775	0.528	FA	0.305	35.2	0.013	0.292	0.696	1.044	0.811
	FA 0.453	9.9	0.029	0.424	0.850	1.068	0.882	FC	0.289	25.6	0.009	0.280	0.712	1.032	0.799
	FC 0.429	7.5	0.022	0.407	0.874	1.054	0.865	FS	0.271	27.3	0.009	0.262	0.730	1.034	0.779
	FS 0.364	5.4	0.013	0.351	0.939	1.037	0.814	20	U 0.418	544.2	0.180	0.238
14	U 1.007	67.8	0.388	0.619	FA	0.194	80.0	0.021	0.173	0.224	1.121	0.602
	FA 0.597	9.2	0.042	0.555	0.410	1.076	0.860	FC	0.187	34.4	0.009	0.178	0.231	1.051	0.612
	FC 0.577	7.7	0.035	0.542	0.430	1.065	0.834	FS	0.164	29.2	0.008	0.156	0.254	1.051	0.570
	FS 0.517	6.7	0.024	0.493	0.490	1.049	0.755	21	U 0.472	651.9	0.223	0.249
15	U 0.983	89.8	0.423	0.560	FA	0.167	53.0	0.014	0.153	0.305	1.092	0.699
	FA 0.668	9.4	0.052	0.616	0.315	1.084	1.156	FC	0.153	28.6	0.007	0.146	0.319	1.048	0.681
	FC 0.617	9.2	0.045	0.572	0.366	1.079	1.032	FS	0.136	30.1	0.007	0.129	0.336	1.054	0.650
	FS 0.551	4.5	0.019	0.532	0.432	1.036	0.938	22	U 0.330	642.8	0.169	0.161
16	U 1.118	409.4	0.811	0.307	FA	0.106	63.4	0.014	0.092	0.224	1.152	0.710
	FA 0.216	9.9	0.014	0.202	0.902	1.069	0.885	FC	0.096	29.1	0.006	0.090	0.234	1.067	0.704
	FC 0.229	13.5	0.020	0.209	0.889	1.096	0.892	FS	0.088	32.5	0.007	0.081	0.242	1.086	0.679
	FS 0.182	12.8	0.014	0.168	0.936	1.083	0.854	C. Red Filter							
17	U 0.851	94.2	0.356	0.495	11	U 0.516	6443.0	0.372	0.144
	FA 0.565	7.8	0.033	0.532	0.286	1.062	1.116	FA	0.070	148.6	0.007	0.063	0.446	1.111	0.821
	FC 0.525	4.9	0.019	0.506	0.326	1.038	1.035	FC	0.074	96.0	0.005	0.069	0.442	1.072	0.832
	FS 0.489	4.3	0.016	0.473	0.362	1.034	0.942	FS	0.063	85.2	0.004	0.059	0.453	1.068	0.814
18	U 1.067	136.6	0.510	0.557	12	U 0.222	2182.0	0.111	0.111
	FA 0.512	15.0	0.051	0.461	0.555	1.111	0.842	FA	0.091	191.1	0.010	0.081	0.131	1.123	0.793
	FC 0.459	6.1	0.019	0.440	0.608	1.043	0.813	FC	0.098	127.7	0.007	0.091	0.124	1.077	0.847
	FS 0.394	6.5	0.016	0.378	0.673	1.042	0.740	FS	0.072	149.1	0.007	0.065	0.150	1.108	0.707
19	U 1.606	105.3	0.871	0.735	13	U 0.640	5776.0	0.412	0.228
	FA 0.682	5.3	0.034	0.648	0.924	1.052	0.909	FA	0.115	205.3	0.015	0.100	0.525	1.150	0.763
	FC 0.683	8.2	0.049	0.634	0.923	1.077	0.896	FC	0.109	153.6	0.008	0.101	0.531	1.079	0.764
	FS 0.590	8.2	0.038	0.552	1.016	1.069	0.826	FS	0.096	95.2	0.005	0.091	0.544	1.055	0.752
20	U 0.674	118.6	0.300	0.374	14	U 0.368	2863.0	0.185	0.183
	FA 0.360	21.0	0.044	0.316	0.314	1.139	0.838	FA	0.119	185.1	0.010	0.109	0.249	1.092	0.714
	FC 0.353	8.3	0.019	0.334	0.321	1.057	0.882	FC	0.123	183.0	0.010	0.113	0.245	1.088	0.728
	FS 0.318	7.4	0.015	0.303	0.356	1.049	0.809	FS	0.108	145.2	0.007	0.101	0.260	1.069	0.693
21	U 0.726	142.7	0.359	0.367	15	U 0.360	3154.0	0.194	0.166
	FA 0.345	13.5	0.028	0.317	0.381	1.088	0.878	FA	0.159	216.3	0.012	0.147	0.201	1.082	0.911
	FC 0.318	6.9	0.014	0.304	0.408	1.046	0.853	FC	0.139	195.2	0.011	0.128	0.221	1.086	0.863
	FS 0.301	7.2	0.014	0.287	0.425	1.049	0.818	FS	0.107	105.0	0.006	0.101	0.253	1.059	0.745
22	U 0.512	180.0	0.282	0.230	16	U 0.542	6969.0	0.402	0.140
	FA 0.225	19.6	0.028	0.197	0.287	1.142	0.898	FA	0.039	98.9	0.004	0.035	0.503	1.114	0.793
	FC 0.218	8.0	0.012	0.206	0.294	1.058	0.922	FC	0.025	124.7	0.005	0.020	0.517	1.250	0.769
	FS 0.184	9.2	0.012	0.172	0.328	1.070	0.829	FS	0.025	114.0	0.005	0.020	0.517	1.250	0.770
B. Green Filter								17	U 0.288	2782.0	0.152	0.136
11	U 0.767	1334.0	0.487	0.280	FA	0.120	166.3	0.009	0.111	0.168	1.081	0.859
	FA 0.170	48.9	0.013	0.157	0.597	1.083	0.798	FC	0.101	92.2	0.005	0.096	0.187	1.052	0.796
	FC 0.171	30.3	0.008	0.163	0.596	1.049	0.806	FS	0.101	88.1	0.005	0.096	0.187	1.052	0.796
	FS 0.146	23.3	0.006	0.140	0.621	1.043	0.777	18	U 0.433	4233.0	0.255	0.178
12	U 0.350	486.6	0.143	0.207	FA	0.120	247.4	0.013	0.107	0.313	1.121	0.782
	FA 0.162	47.5	0.012	0.150	0.188	1.080	0.715	FC	0.091	110.1	0.006	0.085	0.342	1.071	0.733
	FC 0.180	35.9	0.010	0.170	0.170	1.059	0.794	FS	0.063	105.6	0.005	0.058	0.370	1.086	0.680
	FS 0.129	38.0	0.009	0.120	0.221	1.075	0.622	19	U 0.641	6067.0	0.421	0.220
13	U 0.885	1061.0	0.505	0.380	FA	0.123	125.0	0.007	0.116	0.518	1.060	0.802
	FA 0.224	53.1	0.016	0.208	0.661	1.077	0.746	FC	0.127	90.1	0.005	0.122	0.514	1.041	0.811
	FC 0.211	39.1	0.012	0.199	0.674	1.060	0.736	FS	0.118	91.5	0.005	0.113	0.523	1.044	0.799
	FS 0.181	24.6	0.007	0.174	0.704	1.040	0.710	20	U 0.279	2386.0	0.137	0.142
14	U 0.611	459.0	0.225	0.386	FA	0.113	321.6	0.016	0.097	0.166	1.165	0.753
	FA 0.269	45.1	0.016	0.253	0.342	1.063	0.630	FC	0.118	107.2	0.006	0.112	0.161	1.054	0.820
	FC 0.274	45.3	0.016	0.258	0.337	1.062	0.637	FS	0.102	93.3	0.005	0.097	0.177	1.052	0.753
	FS 0.239	35.8	0.011	0.228	0.372	1.048	0.587	21	U 0.306	3061.0	0.171	0.135
15	U 0.590	569.9	0.250	0.340	FA	0.082	165.4	0.008	0.074	0.224	1.108	0.737
	FA 0.326	50.7	0.020	0.306	0.264	1.065	0.880	FC	0.077	90.7	0.004	0.073	0.229	1.055	0.734
	FC 0.302	47.0	0.017	0.285	0.288	1.060	0.817	FS	0.058	97.6	0.004	0.054	0.248	1.074	0.679
	FS 0.251	28.1	0.009	0.242	0.339	1.037	0.718	22	U 0.232	2745.0	0.147	0.085
16	U 0.765	1600.0	0.524	0.241	FA	0.061	217.8	0.010	0.051	0.171	1.196	0.812
	FA 0.094	24.0	0.005	0.089	0.671	1.056	0.775	FC	0.051	87.1	0.004	0.047	0.181	1.085	0.795
	FC 0.092	32.5	0.007	0.085	0.673	1.082	0.771	FS	0.041	110.1	0.005	0.036	0.191	1.139	0.754
	FS 0.075	29.9	0.006	0.069	0.690	1.087	0.753								
17	U 0.507	499.9	0.198	0.309								

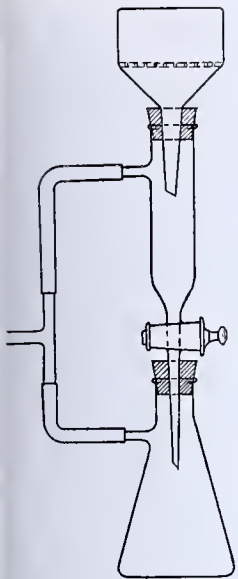


FIGURE 1. FILTERING TUBE

The turbidity (N) figures for the filtrates obtained with all three filtering agents are low, especially in the case of Filter-Cel and silica gel, where they are usually of the same order of magnitude as in a white sugar sirup which has been filtered first with activated carbon, and then through an ultrafilter.

TABLE XII. R -RATIOS, AND DISPERSION QUOTIENTS, BASED ON GREEN FILTER

No.	Unfiltered		R -Ratio for $-\log T$				Dispersion Quotients for N_u			
	Blue	Red	Asbestos filtrate	Blue	Red	Filter-Cel filtrate	Blue	Red	Silica gel filtrate	Unfiltered
11	1.56	0.67	2.22	0.41	2.17	0.43	2.22	0.43	1.54	0.76
12	1.62	0.64	1.95	0.56	1.79	0.54	2.03	0.56	1.76	0.78
13	1.47	0.72	2.02	0.52	2.03	0.51	2.01	0.53	1.53	0.82
14	1.65	0.60	2.22	0.44	2.11	0.45	2.16	0.45	1.72	0.82
15	1.66	0.61	2.05	0.49	2.05	0.46	2.20	0.43	1.69	0.78
16	1.46	0.71	2.30	0.42	2.49	0.27	2.43	0.33	1.55	0.77
17	1.68	0.57	2.05	0.44	2.05	0.40	2.16	0.45	1.80	0.77
18	1.60	0.65	2.06	0.48	2.10	0.41	2.29	0.37	1.52	0.76
19	1.60	0.64	2.24	0.40	2.36	0.44	2.18	0.44	1.51	0.73
20	1.43	0.59	1.86	0.58	1.88	0.63	1.94	0.62	1.67	0.76
21	1.54	0.65	2.07	0.49	2.09	0.50	2.22	0.43	1.61	0.77
22	1.55	0.70	2.12	0.57	2.26	0.53	2.10	0.47	1.67	0.87

The differences between the Filter-Cel and silica gel filtrates, as compared to the asbestos filtrate, are summarized in Table XIII, for both $-\log T$ and C .

TABLE XIII. COMPARISON OF FILTER-CEL AND SILICA GEL FILTRATES

	$-\log T$		C	
	Range %	Average deviation %	Range %	Average deviation %
Filter-Cel vs. asbestos				
Blue screen	+ 6.0 to -10.4	- 3.33	+ 5.7 to - 7.1	- 0.76
Green screen	+11.1 to -12.0	- 4.09	+13.3 to - 8.3	- 1.69
Red screen	+ 7.7 to -35.9	- 7.64	+15.5 to -42.9	- 4.33
Silica gel vs. asbestos				
Blue screen	-11.7 to -23.0	-15.87	- 4.1 to -18.0	-12.93
Green screen	-11.2 to -30.9	-18.27	- 9.8 to -28.4	-16.05
Red screen	- 4.1 to -47.5	-22.03	- 2.6 to -45.8	-19.57

The range in the differences is rather wide for both Filter-Cel and silica gel, owing to selective effects, but the average differences between Filter-Cel and asbestos are rather small, and in the case of C within the limits of error of spectrophotometric analysis, certainly at least in the blue and green. Since it has been shown that asbestos also acts selectively, Filter-Cel may as well be used instead, even by those who believe that asbestos filtration is the correct procedure. If the asbestos pad is packed still more tightly than in these experiments, the results may well fall below those for Filter-Cel. Silica gel gives in all cases lower values than asbestos, and the averages are from 13 to 22 per cent lower.

The selective effect of the three filtering agents is best shown by the R -ratios in Table XII. The ratios vary irregularly from one sugar to another and show no definite trend, proving that the effect of the filtration depends not only on the filtering agent but also on the turbidity and coloring matter present in the sugar itself.

Further examination of the results in Table XI leads to some very important conclusions regarding the mechanism of filtration with all the three agents compared. If we calculate the ratio between $-\log T_f$ (total dispersed material in the filtrate), and C (dispersed material corrected for that portion which causes a Tyndall effect), the figures shown in Table XIV are found.

TABLE XIV. RATIOS BETWEEN $-\log T_f$ AND C

	Range	Average
Asbestos		
Blue	1.05 to 1.14	1.09
Green	1.04 to 1.15	1.08
Red	1.06 to 1.20	1.12
Filter-Cel		
Blue	1.04 to 1.10	1.06
Green	1.03 to 1.08	1.05
Red	1.04 to 1.25	1.08
Silica gel		
Blue	1.03 to 1.08	1.05
Green	1.03 to 1.09	1.05
Red	1.04 to 1.25	1.09

In spite of the fact that silica gel gives much lower values for $-\log T$ and C than either Filter-Cel or asbestos, the average ratios are very much alike for all three, and even the total range, showing the extent of selective action, is not very wide in each case. This shows that even though one filtering agent may remove much more total dispersed material than another, the ratio between turbidity and coloring matter remaining in the filtrates is on the average about the same. This phenomenon has been predicted by Balch: "It is very doubtful whether it is actually possible to remove all the material causing turbidity, if judged by the Tyndall beam, without changing the color of the solution." As the reason for this he gave the fact that the particles causing turbidity are themselves colored, and transmit as well as reflect light selectively.

The results obtained by the writers suggest another, more important reason. It is well known that the intensity of the Tyndall cone decreases with the difference between the refractive indices of the dispersed phase and the dispersion medium, and that the coloring matter in sugar products consists partly of condensation products of sugars—that is, substances of the caramel type, the refractive index of which is about the same as that of sucrose. These coloring matters, of the emulsoid or hydrophylic type, may therefore be expected to produce only a faint or no Tyndall cone, although consisting of particles of the same size as the suspensoids which give a distinct Tyndall cone under the same experimental conditions. But being of the same size, both are filtered out simultaneously. It may therefore be expected that, even though there be no adsorption, each filtering agent, whether it be asbestos, Filter-Cel, or silica gel, will reduce both turbidity and coloring matter to a definite maximum particle size. Silica gel appears to be much more effective in this respect than either asbestos or Filter-Cel, as used by the writers. There is still another possibility. The filtering agents may, because of electrical charges, or for other reasons, act as sensitizers and promote the flocculation of emulsoids in the presence of suspensoids. Silica gel was highly electrified when it was rubbed in a mortar.

Whatever the correct explanation may be, it is evident that filtration with asbestos, Filter-Cel, or silica gel does not remove turbidity, as judged by the Tyndall effect, without removing coloring matter at the same time. The separation of turbidity and coloring matter on the basis of a Tyndall beam

of zero intensity, postulated by the writers, is thus found to be unattainable by filtration methods. In practice, the choice between the three filtering media, when used for the purpose of color determination, becomes therefore merely a matter of arbitrary agreement, which can best be reached by international action. From the practical standpoint, asbestos is the least desirable of the three filtering agents, because its effect depends so largely on its method of preparation and the permeability of the pad, which is very difficult to standardize. Filter-Cel and silica gel are much more promising in this respect because standardized grades of both are commercially available and can be purified very easily. When only color is to be determined, the residual turbidity in the filtrates may or may not be corrected for, as desired. If no correction is to be made, silica gel has the advantage of requiring such a small correction that it may in practice be neglected. In all cases the coloring matter should be expressed in terms of $-\log T$ for a specified dry substance concentration and depth of layer, or better directly as $-\log t$. The quality of the coloring matter may be further characterized by the Q - or R -ratios.

Since there is no actual dividing line between color and turbidity, both varying in particle size and both showing selective absorption and reflection or scattering, it is logical to express turbidity in the same way as the color, according to the practice followed by Balch and by the writers. The latter have shown, however, that the $-\log t$ arrived at by Balch's procedure is merely an optical measure having no direct relation to the turbidity concentration, and that it does not consider the turbidity remaining in the filtrate. In the writers' system, on the other hand, the total turbidity concentration is expressed as the $-\log t$ of an equivalent concentration of a standard turbidity, and the difference in the properties of the turbidity present and of the standard turbidity is characterized by the quality index and by the dispersion quotient of the turbidity. In the preceding paper the quality index was defined as the ratio between the filterable turbidity, $N_u - N_f$, and the turbidity according to Balch. Since this ratio applies only to the filterable turbidity, it is better to use instead that for the total turbidity—that is, the ratio of N_u to $-\log T_u - C$. Similarly, the dispersion quotients should be given for N_u itself rather than for $N_u - N_f$. Both of these changes have been made in the present paper in Tables XI and XII.

Summary and Conclusions

In a study of the factors which affect the simultaneous determination of transmittancy and Tyndall beam intensity of raw sugar solutions with the Pulfrich photometer, it has been found necessary to standardize both the dry substance concentration and the depth of layer of the solution to be measured. A concentration of 60 Brix and a cell thickness of 2.5 mm. have been tentatively adopted. When dark sugar products have to be diluted with white sugar sirup, the two should first be mixed, and the mixture filtered afterward. If they are filtered separately, and the filtrates mixed, the resulting solution is not as good optically as that obtained by the other method. The optical readings should be made about 2 hours after the preparation of the solutions, to allow colloid equilibrium to be established.

Among a number of filtering agents used for the purpose of removing turbidity from raw sugar solutions, asbestos, Filter-Cel, and silica gel have been studied more particularly. It has been shown that all three of these remove both turbidity and coloring matter selectively. Silica gel is most effective in removing total dispersed material. There is little difference in this respect between Filter-Cel and asbestos, provided that the latter is used in the form of a tightly packed pad, but the filtrates obtained with any of the three filtering agents contain turbidity, as judged by the Tyndall effect, and coloring matter in about the same proportions. It is thus not possible to remove turbidity by means of any of them, without removing coloring matter at the same time. The choice thus becomes a matter of agreement. Proposals are made to serve as a basis for such an agreement.

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A New Rubber Particle Count in Hevea Latex

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SO MUCH confusion has grown up in the literature concerning the number of rubber particles in Hevea latex that at the present time there exists a thousandfold error in the currently published reports (1, 3, 8) of the one original determination of this number. Harries (4), Hauser (5), and Noble (8), each reporting the original work of Henri (6), give a count of 50,000,000 particles per cubic centimeter of latex, Harries not specifying the concentration, while Hauser and Noble indicate it to have been 8.7 per cent solids. On the other hand, Dubosc and Luttringer (2), also reporting the work of Henri, record a count of 50,000,000 particles per cubic millimeter in latex of unspecified concentration. The original paper of Henri (6) reported that he had found an average of

50,000,000 particles per cubic millimeter of latex having a specific gravity of 0.973 and containing 8.7 grams of solids per 100 cc. Preliminary counts undertaken by the author with a view to developing a rapid microscopic method for the determination of the dry rubber content of latex indicated that the results of Henri were considerably low. Since the number of microscopically visible particles is a fundamental property of latex, it was felt that a redetermination of this number would be of value.

Experimental Method

PREPARATION OF SOLUTIONS. From 1.0 to 2.0 grams of ammonia-preserved 38 to 40 per cent latex, the solids and dry rubber

content of which had been determined, were weighed by difference, using a medicine dropper, into a 1-liter volumetric flask nearly filled with water to which had been added 15 ml. of 26° Bé. ammonium hydroxide solution to prevent any tendency to flocculation of the latex. The mixture was made up to volume and, after careful shaking, 20 ml. were pipetted out into a 500-ml. volumetric flask almost filled with a filtered 20 per cent sodium chloride solution. The sodium chloride solution was used to stop the Brownian movement of the rubber particles which would render the counting difficult. After being made up to volume with the same salt solution, the necessary amount of the solution, which represents a dilution of the original weight of latex to 25,000 ml., was transferred to the counting chamber using, for convenience, a Thoma blood-diluting pipet.

COUNTING CHAMBER. A Levy counting chamber with the improved Neubauer ruling (9), such as is used in counting blood corpuscles, was used in this work. The counting cell consists essentially of a plane surface of glass containing a centrally located square 1 mm. on a side. This central square millimeter is ruled into 400 equal squares. By means of double marginal rulings these 400 smallest squares are grouped into 25 squares, each containing 16 small squares representing an area of 0.04 sq. mm. Facilities are provided for supporting an optically plane cover glass 0.1 mm. above and parallel with this ruled surface, thus forming a chamber of 0.1 cu. mm. capacity. The volumetric accuracy of the counting chamber is of the order of 4 per cent. One group of 16 of the smallest squares is visible simultaneously with a 4-mm. objective and a 10× Huygenian ocular.

THE MICROSCOPE. A Hartnack and Prasmowski microscope was used. A No. 7 objective, with corrective lens for cover glass thickness, and a No. 3 eyepiece were used in making the counts. This combination of lenses represents a magnification of about 400 diameters. Since no mechanically operated stage was available, it was necessary to provide otherwise for the orderly movement of the counting chamber. This was accomplished by daubing a small quantity of a mixture of 70 per cent rosin and 30 per cent rapeseed oil onto each end of the under surface of the counting chamber, which, by its viscous drag, prevented the capricious movement of the counting chamber when touched by the hand to bring a new group of squares into view. Because the counting chamber depth was great in comparison to the depth of focus of the objective used, it was necessary to focus slowly upwards from the ruled surface of the counting cell to the lower surface of the cover glass in counting each small square in order to assure the inclusion of all the particles. To prevent duplication, the particles were counted only when they came into sharp focus. It was noticed that because the Brownian movement had been stopped there was a pronounced tendency for the particles to settle upwards towards the cover glass and that after the counting chamber had been filled for about 10 minutes fully 75 per cent of all the particles were found in the focal plane nearest the cover glass. Since the boundary lines were least distinct in this focal plane, it was necessary to refill the cell frequently.

THE LATEX. The samples of latex used were obtained from drums of commercial 38 to 40 per cent ammonia-preserved latex. Two of these samples were of the brand known as "No. 4 Plantation Latex," marketed by the Vultex Chemical Company, Cambridge, Mass., and one sample of the brand "Lotol," marketed by the Naugatuck Chemical Company, Naugatuck, Conn.

Results of Counts

The results of the several counts on the different latex samples appear in Table I. The number of particles per gram of latex is the value reported, and for the purpose of comparison among the several samples of latex, which varied slightly in dry rubber content, all the counts are corrected to a common basis of 35 per cent dry rubber content.

TABLE I. RESULTS OF COUNTS

Brand of Latex	Sample No.	Dry Solids %	Dry Rubber Content %	Groups Counted ^a	Particles per Gram ^b
No. 4 Plantation	1	38.4	35.3	2	0.62×10^{12}
	1	38.4	35.3	3	0.65×10^{12}
	1	38.4	35.3	1	0.62×10^{12}
	2	38.5	34.6	4	0.63×10^{12}
	2	38.5	34.6	3	0.60×10^{12}
Lotol	3	39.0	35.9	1	0.64×10^{12}
	3	39.0	35.9	3	0.69×10^{12}

^a Group of 16 small squares.

^b Corrected to 35 per cent dry rubber content.

An average of all the counts recorded in Table I, weighted on the basis of the number of groups counted, gives a figure of 640,000,000,000 rubber particles per gram of latex of 35 per cent dry rubber content. The count of Henri, calculated to the same basis, using the factor 0.92 for conversion from per cent solids to dry rubber content, gives a figure of 218,000,000,000 particles.

Discussion of Results

It must be realized that because there is known to be numerically considerable material of ultramicroscopic proportions in latex which cannot be included in any such particle count as is reported here, but which does contribute slightly to the rubber content of the latex, such a count is inevitably low. If, however, we are willing to neglect the contribution of the ultramicroscopic material to the rubber content of the latex, it is possible to calculate an average particle diameter. In making such a calculation based on the count reported here spherical shape has been assumed for the particles, and a density of 0.914 for the material of the particles was used. On this basis the average rubber particle size in the latex samples used in this investigation is 1.04 microns. The average diameter of the rubber particles of Hevea latex has been determined by Wightman and Trivelli (10), using motion photomicrographs, to be between 0.7 and 0.8 micron. On the other hand, Madge (?) states that "the particles of commercial latex have on an average a diameter of approximately 1.5 microns as measured with a microscope."

Acknowledgment

The author's grateful thanks are due to the Union Paste Company of Medford, Mass., whose facilities and materials were graciously extended for the conduct of this investigation, and to Purcell G. Schube, Boston State Hospital, Boston, Mass., not only for the use of the blood-counting apparatus, but for much helpful advice and many suggestions.

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Determination of Sulfur in Rubber Compounds

I. Precipitation of Barium Sulfate in the Presence of Picric Acid

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THERE is probably no single operation in analytical chemistry that has received more attention from investigators than that of precipitation of barium sulfate by means of a soluble barium salt for the determination of sulfate or of barium. The literature on this subject is voluminous and the conclusions reached by different investigators as to the proper procedure to employ in order to obtain a precipitate which will be filterable and reasonably pure are highly contradictory. The procedure which seems to be in most general use at present for the determination of sulfate is that of adding the barium chloride solution to the hot sulfate solution very slowly, stirring vigorously meanwhile, then allowing the whole to digest at an elevated temperature for several hours before filtering.

The diversity of opinion as to the proper procedure arises, the author believes, from the fact that the barium sulfate precipitate is exceedingly sensitive to its environment and that a very slight change in the amount or kind of impurities present in the solutions during precipitation has a profound effect upon the crystal size and shape of the precipitated particles as well as upon their purity. Kolthoff and Vogelenzang (2) have stated that it is impossible to prescribe a general procedure for the accurate precipitation of sulfate in arbitrary mixtures. In other words, a precipitation procedure which gives satisfactory results in the determination of sulfur in copper ores, for instance, may not yield a satisfactory precipitate when applied to the determination of total sulfur in hard rubber dust, and a study of each type of determination, with due consideration for the amount and kind of impurities present, must be made in order to find the conditions necessary to obtain a precipitate which is pure and easily filterable.

For several years it has been known to a few analysts that the presence of picric acid in the sulfate solution at the time of precipitation would yield a precipitate which could be filtered immediately without the necessity of prolonged digestion before filtration. This bit of information has not appeared in the literature, although Dubrisay and Toquet (1) in 1919 suggested the use of phenol; and at present picric acid is being used in a number of laboratories throughout the country. Thus, the author does not claim in any sense that the use of picric acid is original with him, but presents this study in the hope that its use will become as widespread as it deserves.

The technic employed in the use of picric acid is simple. From 1 to 5 cc. of a saturated solution of picric acid in water are added to the acidified sulfate solution and stirred in before adding the barium chloride. The barium chloride may be added quickly, as nothing is gained by adding it slowly. After adding the barium chloride (which should be in excess as small as practicable) the solution should be gently boiled for from 5 to 10 minutes. It will then be ready to filter. In case the sulfate solution contains large quantities of sodium salts, as in sulfur determinations on Parr peroxide bomb residues, or strong oxidizing acids, as in the perchloric acid method for total sulfur in rubber compounds, the amount of picric acid necessary to produce the desired effect may be greater than that given above and in these cases from 10 to 25 cc. of the saturated solution should be used.

In the company's laboratories, picric acid has been in constant use for the past 8 years in the determination of free sulfur in rubber compounds by the bromine-oxidation method and of total sulfur by oxidation with perchloric acid. It has been known all this time that its use greatly improved the filtra-

bility of the precipitated barium sulfate without deleterious effect on the quantitative results, but no systematic study of the phenomenon was made until within the last few months.

When the use of picric acid was first under consideration, a long series of parallel determinations showed that the quantitative results obtained with and without picric acid were, if not identical, at least within the limits of accuracy of the methods of analysis themselves. These observations have been confirmed in the recent study, as shown in Table I, which gives the results obtained using pure solutions of sulfuric acid as the source of sulfate ions. In each case, the numerical result given is the average obtained from determinations run in triplicate.

TABLE I. PRECIPITATION OF BARIUM SULFATE

No.	Water Cc.	0.1 N H ₂ SO ₄ Cc.	Picric Acid Cc.	10% BaCl ₂ Cc.	Bromine Cc.	BaSO ₄ Gram
1	100	20	0	15	0	0.2333
2	100	20	1	15	0	0.2359
3	100	20	0	15	3	0.2337
4	100	20	1	15	3	0.2364
5	400	20	0	15	0	0.2355
6	400	20	1	15	0	0.2358
7	250	4	0	10	3	0.0457
8	250	4	1	10	3	0.0464
9	400	1	0	1	0	0.0105
10	400	1	1	1	0	0.0105

In each case, the result obtained where picric acid is present is slightly higher than where it is absent. When the gravimetric factor for converting barium sulfate to sulfur (0.13136) is applied to this difference, it is divided by approximately 7.3 and becomes smaller than the usual difference between duplicate determinations, although it is always positive in sign. These results removed any fear that picric acid might increase the solubility of barium sulfate and cause incomplete precipitation.

Runs 3 and 4 differ from 1 and 2 in the fact that before the barium chloride was added 3 cc. of bromine were added, allowed to stand for 30 minutes, and then boiled off, after which the picric acid was added and the precipitation performed as usual. This was done to determine whether bro-

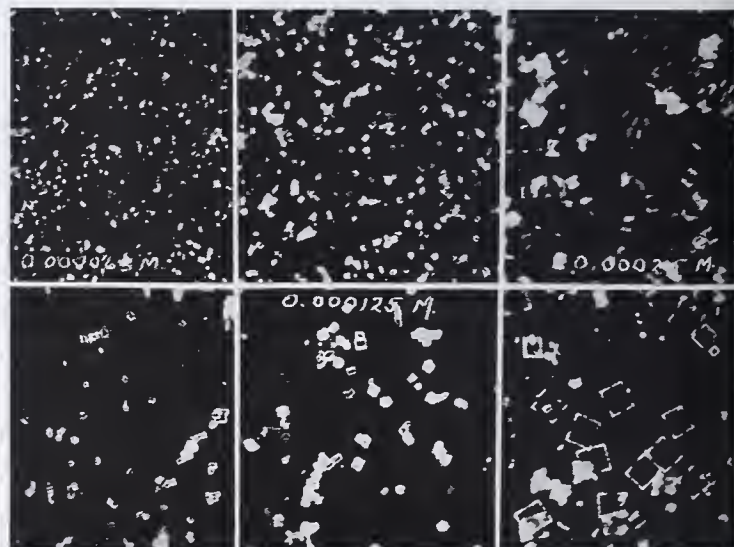


FIGURE 1

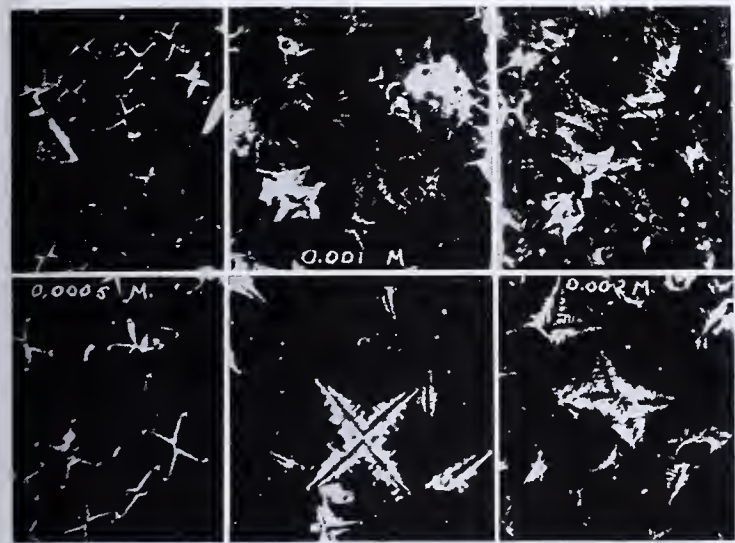


FIGURE 2

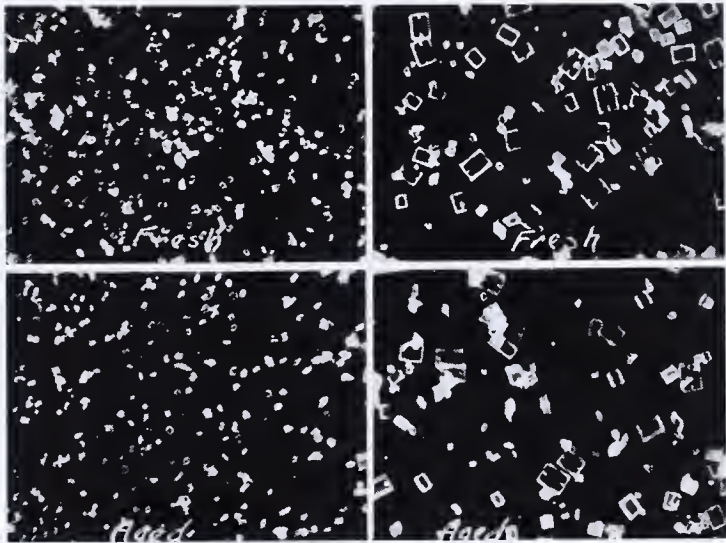


FIGURE 3

mine or hydrobromic acid would have any appreciable effect upon the result, which is apparently not the case. Runs 7 and 8 are in approximately the range of concentration which is encountered in free sulfur determinations on nonblooming tire stocks. Runs 9 and 10 are very dilute, and the excess of barium chloride is low in concentration. The exact agreement obtained in these last runs would make it appear that the differences in results obtained in the previous runs were due to increased occlusion or adsorption of barium chloride brought about in the presence of picric acid. The results given in Table II show that this probably is the case.

TABLE II. PRECIPITATION OF BARIUM SULFATE

No.	Water Cc.	0.1 N H ₂ SO ₄ Cc.	Picric Acid Cc.	0.5 N BaCl ₂ Cc.	BaSO ₄ Gram
1	250	25	0	20	0.1163
2	250	25	1	20	0.1161
3	100	20	0	15	0.0870
4	100	20	1	15	0.0873

In these runs, the barium chloride present was insufficient to react with all the sulfuric acid present, so that there was no excess, but rather a deficiency of barium chloride. The results are well within the limits of accuracy of the ordinary volumetric buret and the differences are opposite in sign in the two pairs of runs, which differ considerably in concentration, runs 3 and 4 being twice as concentrated as runs 1 and 2.

Since we now have very good evidence that picric acid increases the adsorption of barium chloride by barium sulfate, to a very small extent, it was logical to believe that it might have a similar effect upon other ions which might be present as impurities in the solution. Since iron is commonly present in solutions from which barium sulfate is precipitated, a pair of runs was made in which ferric chloride was present. After filtering the precipitates obtained, they were analyzed and the iron was determined. The results are shown in Table III.

TABLE III. DETERMINATION OF IRON

No.	Water Cc.	0.1 N H ₂ SO ₄ Cc.	1% Picric Acid Cc.	10% BaCl Cc.	15% FeCl ₂ Cc.	Fe in BaSO ₄ Gram
1	250	25	0	10	2	0.057
2	250	25	5	10	2	0.0051
3	250	25	0	10	2	Faint trace
4	250	25	5	10	2	Faint trace

In runs 1 and 2 an appreciable amount of iron was picked up. It had been foreseen that iron might be adsorbed by the filter paper, so extraordinary precautions were taken in wash-

ing. The filters were washed at least 30 times with boiling water and the washings tested colorimetrically for iron. In the last 5 or 6 washings no iron was detectable, yet the appearance of the ignited barium sulfate led to the belief that the filter paper itself was responsible for a considerable portion of the total iron present. Accordingly, runs 3 and 4 were made, using fritted glass filters instead of paper for the final filtration. The precipitate was then removed from the filter and analyzed for iron as before. This time, the colorimetric test for iron was so faint as entirely to prevent its quantitative estimation.

Table IV shows the results obtained in actual free sulfur and total sulfur determinations. These figures are typical of those obtained from hundreds of comparison determinations made during the last 8 years.

TABLE IV. RESULTS IN ACTUAL SULFUR DETERMINATIONS

Sample	Sulfur without Picric Acid %	Sulfur with Picric Acid %
156A (free sulfur)	0.35	0.37
	0.35	0.37
159	0.40	0.40
	0.40	0.40
160	0.32	0.33
	0.32	0.33
1 (total sulfur)	1.944	1.946
2	2.561	2.562

That the effectiveness of picric acid in increasing the ease of filtration is due to an actual increase in particle size of the barium sulfate crystals and not to any coagulating effect of the reagent is illustrated in the accompanying photomicrographs.

Figures 1 and 2 show the crystals obtained from sulfuric acid solutions of various concentrations. In Figure 1, upper row, the concentrations were 0.000063 M, 0.000125 M, and 0.00025 M, respectively, reading from left to right. The lower row shows the precipitates obtained from solutions of the same concentrations, containing in addition 0.0025 per cent of picric acid. The precipitates in the first two photographs, top row, were not entirely held up by a Carl Schleicher Schull 589 Blue Ribbon filter, while all the precipitates formed in the presence of picric acid were held up completely by this grade of paper. In Figure 2, the concentrations of the solutions were 0.00050 M, 0.001 M, and 0.002 M, respectively, the lower row containing the same amount of picric acid as in Figure 1. In all these experiments, the precipitates prepared without picric acid were digested at 80° C. for 16 hours before photographing, while those prepared with picric acid were photographed immediately after precipitation.

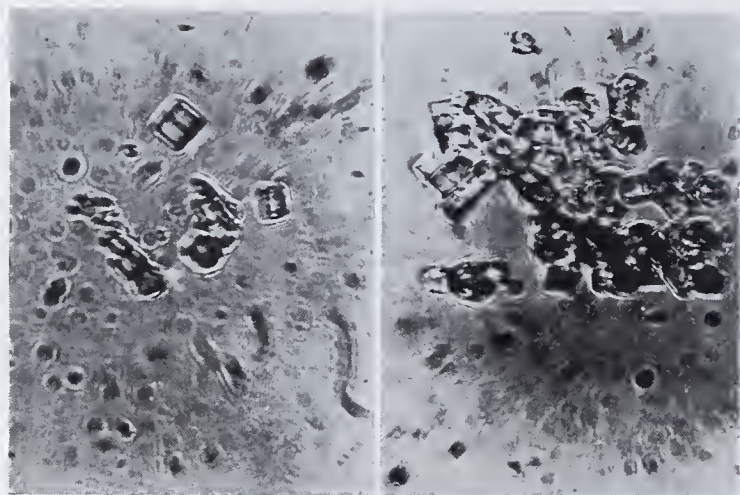


FIGURE 4



FIGURE 6

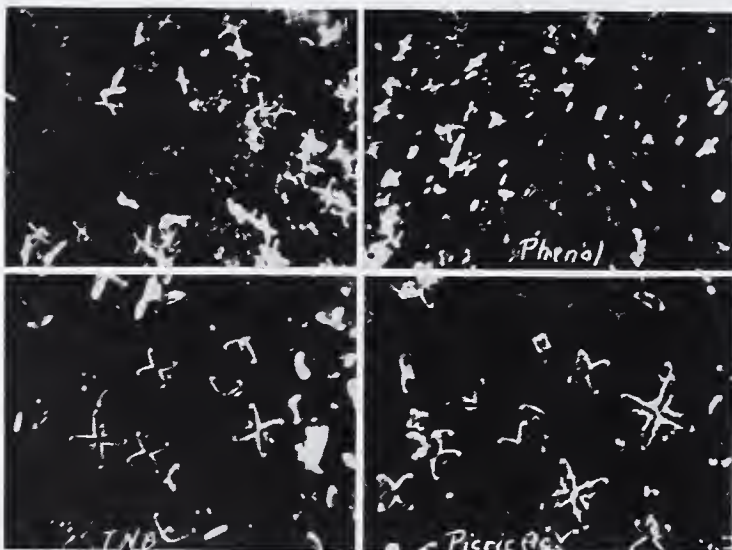


FIGURE 7

In this connection it was interesting to note that digestion of the barium sulfate for 16 hours at a temperature of 80°C . had no significant effect upon the particle size. In no case could any change in particle size be detected until the digestion had progressed for several days. There is a generally accepted belief that during digestion the smaller crystals tend to pass into solution, while the larger crystals grow still larger at the expense of the smaller ones. There is no doubt that this process will take place if sufficient time be given, but it is much too slow to have any appreciable effect during the usual overnight digestion.

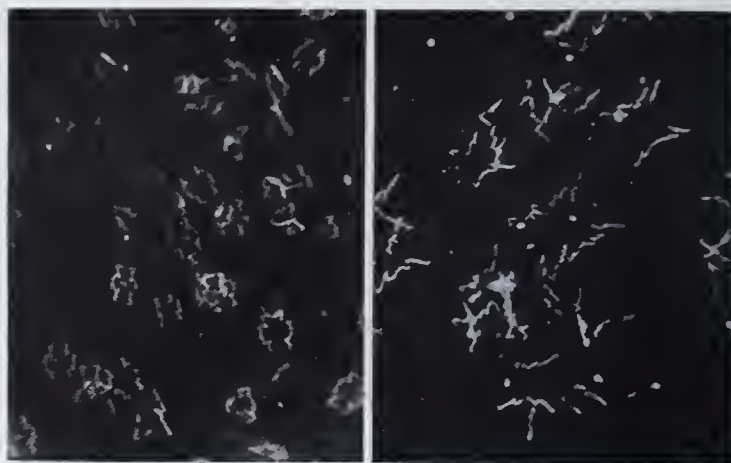


FIGURE 5

Figure 3 shows the appearance of fresh precipitates, without and with picric acid (top row), and the same precipitates after 16 hours' digestion (bottom row). There is no perceptible difference in the crystal size of the fresh and aged precipitates. Since there can be no doubt that overnight digestion does improve the filterability of barium sulfate, some other process must take place and a further investigation showed that there occurred a cementation of the individual particles into larger groups or aggregates as shown in Figure 4. On the left is shown the fresh precipitate and on the right the same precipitate after 16 hours' digestion, special precautions having been taken to prevent the breaking up of the rather loosely cemented aggregates in mounting them on the microscope slide. This process of aggregation has also been observed by other investigators, notably Trimble (3) of the University of Oklahoma.

Figure 5 shows the appearance of the precipitates obtained in a regular free sulfur determination by the bromine-oxidation method, without and with picric acid, respectively. In Figure 6 are shown the precipitates obtained in the determination of total sulfur by oxidation with perchloric acid. Figure 7 shows the effect of materials other than picric acid. The upper left photograph shows the crystals obtained from pure sulfuric acid and barium chloride solutions; those in the upper right were precipitated in the presence of approximately 0.5 per cent of phenol; those in the lower left were precipitated from a saturated solution of trinitrobenzene; while those in the lower right were precipitated in the presence of 0.0025 per cent of picric acid. In the presence of phenol, the crystals are actually decreased in size. Trinitrobenzene increases the particle size to some extent, but its low solubility in the aqueous solution probably prevents its being as effective as picric acid.

It has been the author's experience that, in every case, the particle size of the barium sulfate precipitates has been materially increased by the presence of picric acid. It is not recommended in any sense as a cure-all for filtration troubles with barium sulfate, but its use will save a great deal of time and trouble if properly applied to the particular type of sulfur determination in question.

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- (2) Kolthoff, I. M., and Vogelenzang, E. H., *Pharm. Weekblad*, **56**, 122-42 (1919).
- (3) Trimble, H. M., *Proc. Oklahoma Acad. Sci., Univ. Oklahoma Bull.*, New Series No. 409, Studies Series No. 29, 197 (1928).

RECEIVED October 14, 1935. Presented before the Division of Rubber Chemistry, Akron, Ohio, October 1, 1935.

(Part II follows)

II. Sources of Error in the Determination of Free Sulfur in Rubber Compounds Containing Rapid Accelerators and Sulfur Bearing Accelerators

IT HAS been known for many years that the classic analytical methods for determining the degree of vulcanization of rubber stocks—namely, determination of the combined sulfur directly on an acetone-extracted sample, or indirectly by determining the free sulfur and subtracting it from the total sulfur—possessed certain inherent errors. In the older types of stocks, using relatively slow accelerators, those errors were either too small to be disturbing or could be compensated for by fairly simple calculations, taking into consideration the amounts of sulfur-bearing ingredients such as lithopone, barytes, rubber substitute, mineral rubber, etc., known to be in the stock. Furthermore, the physical properties of the stocks had been cataloged in the minds of the compounders by long experience, as fairly simple functions of the temperature and time of cure. Hence, little attention was paid to these errors in sulfur determinations, and the compounder could obtain a fairly good mental picture of the state of cure from the total sulfur and free sulfur results furnished him by the laboratory.

Of late, however, the picture has been changed by the introduction and widespread use of sulfur-bearing accelerators and of accelerators of the “ultra” and “semi-ultra” type. The compounder has found that he must accustom himself to physical properties which no longer vary as simple functions of the temperature and time of cure, and the analyst finds that the free sulfur which he still tries to determine by the bromine-oxidation method is no longer simply elemental sulfur which failed to react with rubber during the vulcanization process, but may be in the form of a number of other things enormously more complicated. Furthermore, he may find that extraction with acetone—the foundation upon which his free sulfur determination rests—is not the clean-cut solvent operation that it was in the days before the more rapid accelerators came into common use.

The American Society for Testing Materials defines “free sulfur” as “that which is removed during acetone extraction” (1). No explanation is given as to whether this definition shall be construed to mean all sulfur extracted by acetone or only the elemental sulfur.

Free sulfur determinations on stocks containing rapid accelerators or sulfur-bearing accelerators are subject to the following errors:

1. Elemental sulfur introduced into the compound as an impurity in the accelerator
2. Sulfur in the molecule of the accelerator
3. Sulfur in the acetone-soluble products of the vulcanization reaction
4. Sulfur in acetone-insoluble combinations other than with rubber
5. Curing of the stock during extraction with acetone

These sources of error are, of course, in addition to the sources of error found in the older types of compounds—namely, combination of a part of the elemental sulfur with resins and with various fillers to form sulfides, introduction of sulfur into the stock in fillers such as barytes, rubber substitute, etc.

The first source of error—elemental sulfur occurring in the accelerator as an impurity—is probably the smallest and least disturbing of all. The commercial sulfur-bearing accelerators may contain 6 per cent or even more of elemental sulfur, but its net effect is simply a change in the total elemental sulfur as shown in the recipe. Because of the small amounts of accelerator usually used, this change is small.

Items 2, 3, and 4—sulfur in the accelerator molecule, sulfur

in the acetone-soluble, and in the non-acetone-soluble products of the vulcanization reaction—are closely related and may be considered together. For simplicity in explanation, let us see the effect of these three sources of error on the results of sulfur determinations on stocks containing a specific accelerator—mercaptobenzothiazole (MBT). This material contains two atoms of sulfur in the molecule: a mercapto sulfur or —SH group and a ring sulfur in the thiazo group.

Upon treatment with bromine, as in the bromine-oxidation method for free sulfur, the mercapto sulfur is readily oxidized and appears in the result. The ring sulfur is not appreciably oxidized and is lost unless a more drastic oxidizing agent such as perchloric acid is used. Thus, of whatever unchanged mercaptobenzothiazole in the cured stock goes into the acetone extract, approximately half of its sulfur (the mercapto sulfur) appears in the result. The amount of unchanged mercaptobenzothiazole present in a cured stock is a function of various factors, such as time of cure, composition of the stock, etc., and so long as any unchanged mercaptobenzothiazole is present which can go into the acetone extract (and it is probably always present, no matter how long the cure) there is a positive error in determining the extracted sulfur. This error is dependent, among other things, on (1) mercaptobenzothiazole-sulfur ratio in the recipe—that is, the lower the proportion of sulfur, the greater will be the error—and (2) the extent of the cure, which progressively removes a part of the mercaptobenzothiazole as a source of sulfur available for oxidation with bromine.

It is possible that the mercaptobenzothiazole-sulfur ratios at various stages of a cure can be such that the acetone-extractable sulfur due to the accelerator may be several times greater than the actual amount of elemental sulfur. Table I, illustrating such a condition, shows results obtained from a stock containing rubber 100, zinc oxide 5, stearic acid 1, MBT 3, and sulfur 0.5 parts.

TABLE I. DETERMINATION OF SULFUR

Cure, at 25 pounds (130.4° C.), min.	Raw	30	45	60	240
Free sulfur, bromine method, %	0.82	0.37	0.30	0.29	0.21
Elemental sulfur, %	0.50	0.128	0.046	0.059	0.045
Difference, %	0.32	0.242	0.254	0.231	0.165
MBT in acetone extract, %	2.91	2.28	1.95	1.80	1.64

The elemental sulfur was determined on the stock by the method of Guppy (2), which does not appreciably decompose mercaptobenzothiazole in the short time required for the determination, while the mercaptobenzothiazole determinations were made by precipitation of its copper salt from benzene solution by means of copper oleate.

From these results it is obvious that the error due to mercapto sulfur is by no means constant. The numerical error is progressively smaller but proportionally larger as the cure increases and the extractable mercaptobenzothiazole decreases. With such proportions of curing ingredients, it is of such magnitude as seriously to affect the result, especially in long overcures. In the cures above 30 minutes, the elemental sulfur has practically disappeared, yet the “free sulfur” is still appreciable.

Regarding the sulfur compounds present in the acetone-soluble products and in the acetone-insoluble products of the vulcanization, very little is known except that they exist. It is not unlikely that during the cure, the mercapto group splits off from some of the mercaptobenzothiazole, leaving the benzothiazole group either combined with other sub-

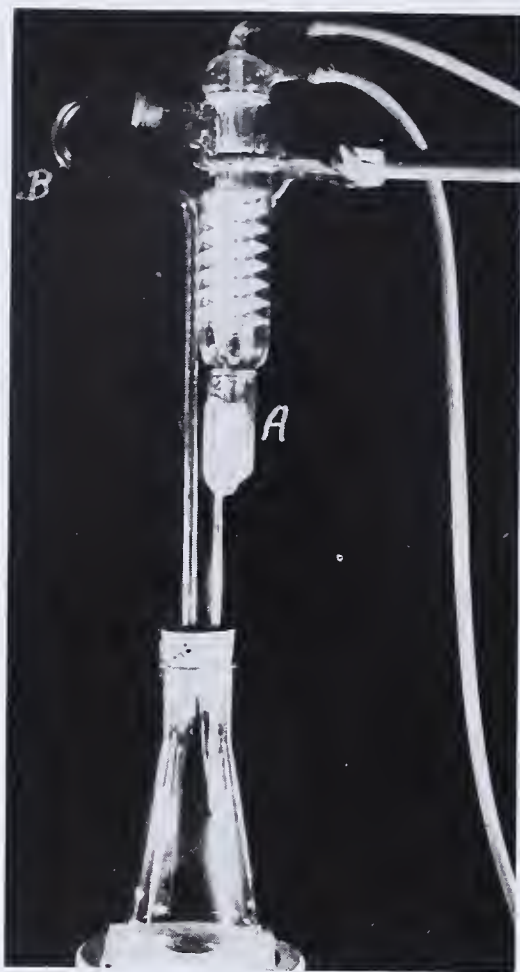


FIGURE 1

stances, split up in various ways or in the form of metallic complexes. Some of these reaction products may be readily soluble in acetone, others very difficultly soluble, and removed only by very prolonged extraction, while still others are not removed by acetone at all. These last, unless removed by some solvent other than acetone, remain in the extracted sample, later to appear as "combined" sulfur upon oxidation with perchloric acid.

The last item of error—cure during the extraction with acetone—is probably the largest of all, and is certainly the most disturbing, since it eliminates at one stroke all analytical methods which depend upon the accepted methods of acetone extraction. The extraction maintains the sample at a temperature of 57° C. (135° F.) and many accelerators cure noticeably at this temperature, while some may even be activated somewhat by the acetone. An indication of the significance of this phenomenon will be seen in Table II, which shows the results obtained by the regular extraction and bromine-oxidation method and by Guppy's method on a stock containing rubber 100, zinc oxide 5, stearic acid 1, MBT 0.5, and sulfur 3 parts.

TABLE II. COMPARATIVE RESULTS

Cure, at 25 pounds (130.4° C.), min.	Raw	30	45	60	240
Free sulfur by extraction and bromine oxidation, %	2.37	0.73	0.37	0.20	0.06
Elemental sulfur by Guppy's method, %	2.42	0.85	0.44	0.29	0.06

Here, it will be seen that the elemental sulfur result is higher than the "bromine free sulfur" result, even though the bromine oxidation gives the elemental sulfur plus the mercapto sulfur in the acetone extract. In other words, sufficient cure has taken place in the process of extraction to make the bromine free sulfur appear lower than the elemental sulfur, in spite of the positive error due to the mercapto sulfur.

Various methods have been tried to prevent, or at least reduce, the magnitude of this cure during extraction and the most effective method so far developed has been that of cold extraction—that is, by using an apparatus in which the acetone is cooled to or below room temperature before coming in contact with the sample. The apparatus used was one built up of glassware available in most laboratories and is shown in Figure 1.

The sample is placed in the siphon cup, A, which is an ordinary Pyrex cup having an extension sealed to the lower end of the siphon, so as to give it sufficient length to pass through a cork stopper which is placed in the regular A. S. T. M. extraction flask. The vapor tube, B, carries the acetone vapors from the flask to the top of a Friedrich condenser, through which the condensed vapors pass, cooling the acetone to approximately tap-water temperature before it comes in contact with the sample. The top of the siphon cup is in loose contact with the bottom of the condenser, thus keeping evaporation at a minimum and at the same time allowing sufficient venting for the apparatus. The sample is extracted on this apparatus for 16 hours and then is transferred to a regular A. S. T. M. siphon cup, and the flask with its contents is removed from the stopper and placed on the customary hot plate where the extraction is continued, hot, until complete. Thus the first stage removes a large portion of the curing ingredients without heating the sample to a curing temperature, and the process is finished at the higher temperature to insure complete extraction.

In Table III is shown the effect of such an extraction upon the combined sulfur.

TABLE III. EFFECT OF COLD EXTRACTION

Stock	Z-516	Z-517
Rubber	100	100
Zinc oxide	5	5
Stearic acid	1	1
MBT	0.5	3
Sulfur	3	0.5
Total sulfur, elemental and in MBT, calculated, %	2.914	1.505
Combined sulfur, left by hot extraction of raw stock, %	1.09	0.44
Combined sulfur, left by cold extraction of raw stock, %	0.05	0.19

Thus, with the present bromine method the "free sulfur" determined is actually the elemental sulfur plus a more or less indefinite fraction of the sulfur in the accelerator molecule and minus the sulfur lost in cure during extraction. Therefore, the definition given for free sulfur and the method given for its determination are incompatible, and until the definition is changed to remove its ambiguity and the method changed to fit the revised definition, the rubber analyst is left in a rather embarrassing position with regard to this very important determination.

Literature Cited

- (1) A. S. T. M. Standards, p. 1135 (1933).
- (2) Guppy, W. D., *Rubber Chem. Tech.*, 5, 360-2 (1932).

RECEIVED October 14, 1935. Presented before the Division of Rubber Chemistry, Akron, Ohio, October 1, 1935.

CORRECTION. In the article "A Thermionic Titrimeter without Batteries," by Willard and Hager, which was published in the ANALYTICAL EDITION for March 15, 1936, the sentence beginning at the bottom of page 144 and running over to the top of page 145 should read as follows: "Since the power requirements are low, any good radio power transformer designed for midget sets and capable of delivering 10 ma. at 220 volts for the plates of the tubes and 2 amperes at 2.5 volts for the heater will be satisfactory." The third sentence in the second paragraph under the heading "Variable Resistor" in the same column should read: "The settings of R_3 and R_4 have no bearing on the accuracy or sensitivity of the titrimeter, but the values of R_3 and R_4 for maximum sensitivity depend on the effective resistance of the tubes and of the meter...."

Iodometric Determination of Maltose

A Rapid and Convenient Semi-micromethod for Determining Maltose in Studies of Amylase Action

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THE method briefly presented here for the iodometric determination of reducing sugar formed in the hydrolysis of starch by amylases was developed to meet the special requirements of studies of amylase action in the presence of heavy water (5) but has proved convenient for more general use with these enzymes. The method is accurate, precise, and rapid, requires relatively small volumes of solutions and no elaborate apparatus, and is suited to work with different amylases. This is shown by the quantitative recovery of maltose from starch dispersions of different electrolyte concentrations and hydrogen-ion activities adjusted to the conditions which favor the action of pancreatic amylase (11) on the one hand and of the amylases of barley malt (4, 12) on the other. The method is especially recommended for work with heavy water, in which the recovery of the heavy water is an important consideration, as its dilution with reagents is kept relatively low and its evaporation is decreased by the omission of such steps as boiling and filtering which are encountered in many other procedures.

Previous investigators have emphasized the importance of quantitative interpretation of controlling the hydrogen-ion activity of the solutions during the oxidation of sugar by iodine (1-3, 6-8) and have proposed the use of suitable buffers (2, 3, 7, 8). This principle has been successfully applied in the micromethod recently developed by Linderström-Lang and Holter (7) for the determination of minute amounts of reducing sugar in microstudies of amylase action and has been incorporated in the method described here. The present report does not introduce new theoretical principles but unites in one convenient procedure conditions which have been found important by different workers.

Determination of Reducing Sugar

REAGENTS. A buffer solution (7) was prepared by mixing 5 volumes of 0.2 M sodium carbonate and 1 volume of 0.4 M hydrochloric acid. The sodium carbonate was purchased in the form of a highly purified and analyzed product and used without further purification.

0.05 M iodine in 2.4 per cent potassium iodide (14), 0.6 M sulfuric acid, 0.05 M sodium thiosulfate, and 1 per cent starch dispersion as indicator.

PROCEDURE. Five cubic centimeters of the buffer solution are pipetted into a 250-cc. glass-stoppered Erlenmeyer flask. One cubic centimeter of the sugar solution (starch-hydrolysis mixture) to be analyzed is pipetted into the buffer solution in the flask and immediately treated with 2 cc. of 0.05 M iodine solution which is added from a long-tipped automatic buret graduated to 0.01 cc. After gentle rotation to insure thorough mixing, the solution is allowed to stand in the tightly stoppered flask in the dark at room temperature for 30 minutes for the oxidation of the sugar. Variations in room temperature from 23° to 29° do not appreciably influence the results. The time allowed for the oxidation of the sugar is, however, important and should be kept constant. At the end of 30 minutes, 5 cc. of 0.06 M sulfuric acid are added from a buret in such a manner as to wash down the sides of the flask and mix gently but thoroughly with the solution. The excess iodine is immediately titrated with 0.05 M thiosulfate which is added from an automatic long-tipped buret graduated to 0.02 cc. If no starch is present, 1 or 2 drops of a 1 per cent starch dispersion are added as indicator. The difference between the volume of thiosulfate required to reduce 2 cc. of the original iodine solution, treated as described above, and that required for the iodine which remains after the oxidation of the sugar repre-

sents the iodine reduced by the sugar and, hence, gives the equivalent of maltose present in the solution.

The data presented here indicate that the maltose is quantitatively oxidized under the prescribed conditions (pH approximately 9.9) to the corresponding monobasic acid according to the following equation:



With the type of buret suggested, approximately 1 minute is required to combine the sugar solution with the buffer and the iodine, while 2 minutes are sufficient for the addition of the sulfuric acid and the titration with the thiosulfate. This makes it possible to obtain measurements of maltose at frequent intervals, 2 or 3 minutes apart, and enables one to follow the course of the formation of maltose throughout the hydrolysis of starch by amylase or to obtain strictly comparable measurements of the action of a given enzyme solution upon different substrates hydrolyzed side by side. In cases where frequent sampling of hydrolysis mixtures is desired, the aliquots of the buffer solution are pipetted into the glass-stoppered Erlenmeyer flasks before the enzyme hydrolyses are started.

ACCURACY. The accuracy of the method was established by the use of a purified sample of maltose. It was found to contain 94.9 per cent of maltose when examined by the gravimetric copper-reduction method of Quisumbing and

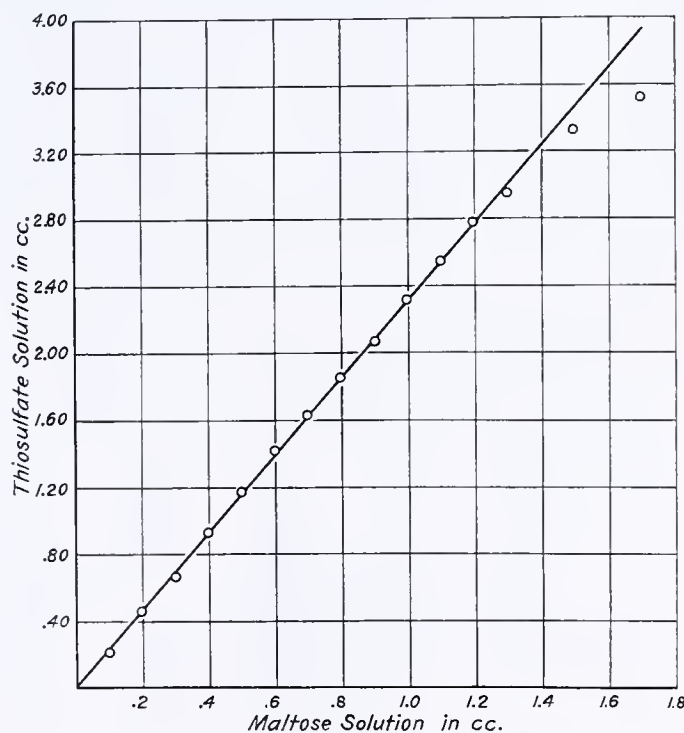


FIGURE 1. RECOVERY OF MALTOSE FROM ITS AQUEOUS SOLUTIONS

Data represent thiosulfate equivalent to the iodine reduced by the maltose. Circles show experimental values; solid line, the stoichiometric values. The maltose solution contained approximately 20 mg. of anhydrous maltose per cc. The thiosulfate solution was 0.0516 M (1 cc. was equivalent to 0.0877 mg. of anhydrous maltose).

Thomas (9); 95.1 per cent of maltose when examined for specific rotatory power, $[\alpha]_D^{20} = 131.29^\circ$ (10); and 94.9 per cent of maltose when examined by the method outlined here.

PRECISION. The precision or reproducibility of the method is shown by the following typical data: Eight aliquot portions of 1 cc. each of a maltose solution which contained approximately 20 mg. of maltose per cc. were treated as described above. The 0.05 *M* thiosulfate required to reduce the excess of iodine which remained after the oxidation of the sugar in the different aliquots was 2.11, 2.11, 2.11, 2.11, 2.10, 2.11, 2.11, and 2.11 cc. (0.01 cc. of the thiosulfate solution used was equivalent to 0.085 mg. of anhydrous maltose).

LIMITS OF CONCENTRATION OF MALTOSE. The stoichiometric relationship between maltose and iodine given above was established with 1-cc. portions of aqueous solutions of maltose which contained approximately 20 mg. of maltose per cc. By taking the experimental thiosulfate equivalent of 1-cc. portions of such maltose solutions as 100 per cent recovery of maltose, it was found that the method outlined here may be used for the quantitative determination of maltose up to 25 mg. This is shown by the experimental data and calculated values given in Table I and in Figure 1. When not more than 25 mg. of maltose are considered, the average deviation of the differences between the experimental and stoichiometric values (columns 3 and 4, Table I) is 0.01 cc. of the thiosulfate solution, equivalent to 0.0877 mg. of anhydrous maltose. Therefore the method is suitable for the determination of the amounts of maltose which are theoretically obtainable from 1-cc. portions of reaction mixtures resulting from the hydrolysis of 1 or 2 per cent starch.

DETERMINATION OF MALTOSE IN THE PRESENCE OF STARCH AND ITS HYDROLYSIS PRODUCTS. In the study of amylase action it is important to use a method for the determination of reducing sugar which gives quantitative results in the presence of starch and its other hydrolysis products, which may be present in the reaction mixtures in any proportions depending upon the conditions of the amylase experiments. The procedure outlined above fulfills these requirements. The typical data summarized in Table II show that the presence of 2 per cent starch and of the electrolytes and hydrogen-ion activities which favor the action of pancreatic amylase on the one hand (11) and of the amylases of barley malt on the other (4) do not interfere with the accurate determination of maltose and justify the use of the method for the study of different amylases which act upon starch adjusted to widely different conditions (4, 11). Moreover, the data summarized in Table III show that maltose was quantita-

tively accounted for when it was superimposed upon reaction mixtures obtained at different stages of the hydrolysis of starch, in the presence of different concentrations and proportions of its hydrolysis products. This justifies the use of the method to follow the course of the formation of maltose from starch throughout its hydrolysis by amylase.

TABLE II. DETERMINATION OF MALTOSE IN PRESENCE OF 2 PER CENT STARCH ADJUSTED TO CONDITIONS WHICH FAVOR ACTION OF DIFFERENT AMYLASES

(Data expressed in cc. of 0.05 *M* thiosulfate required for reduction of excess iodine)

	<i>a</i>	<i>b</i>	
1 cc. of maltose solution, alone			1.89
1 cc. of 2 per cent starch, alone	4.36	4.36	..
1 cc. of 2 per cent starch + 1 cc. of maltose solution	1.88	1.88	..
0.5 cc. of maltose solution, alone			3.15
1 cc. of 2 per cent starch + 0.5 cc. of maltose solution	3.08	3.07	..

^a 2 per cent starch adjusted to pH 7.1; 0.01 *M* phosphate; 0.025 *M* sodium chloride; conditions which favor the action of pancreatic amylase (11).

^b 2 per cent starch adjusted to pH 4.5; 0.01 *M* acetate; conditions which favor the action of the amylases of barley malt (4).

In this connection, it is of interest to note that there is good agreement in the values obtained for reducing sugar (calculated to maltose) formed in the hydrolysis of starch by amylase when comparable reaction mixtures are analyzed by the method described above and by the gravimetric copper-reduction procedure heretofore generally employed in this laboratory (11, 13). In a typical case, proportionate volumes of a solution of pancreatic amylase reacted with 100-cc. and 5-cc. portions of 2 per cent buffered (11) starch. At the end of 30 minutes, the 100-cc. digestion mixtures, when examined by the gravimetric method, yielded 270 mg. of maltose, while 1-cc. aliquots of the 5-cc. reaction mixture gave 2.79 mg. of maltose per cc. when analyzed by the procedure described here.

TABLE III. RECOVERY OF MALTOSE

(When superimposed on reaction mixtures at different stages of the hydrolysis of starch by pancreatic amylase)

Time of Hydrolysis of Starch by Amylase	Reaction mixture alone	Thiosulfate for Residual Iodine	
		Reaction mixture plus 1 cc. of maltose soln. ^a	Difference ^a
<i>Min</i>	<i>Cc.</i>	<i>Cc.</i>	<i>Cc.</i>
10	3.00	1.96	1.04
20	2.77	1.76	1.01
45	2.59	1.58	1.01
60	2.52	1.51	1.01
120	2.48	1.43	1.05

^a 1 cc. of this maltose solution alone was equivalent to 1.01 cc. of the thiosulfate solution.

TABLE I. RECOVERY OF MALTOSE FROM AQUEOUS SOLUTIONS OF KNOWN CONCENTRATION

Maltose Solution Used	Thiosulfate for Residual Iodine	Thiosulfate Equivalent to Maltose Oxidized		Maltose Recovered	
		Experimental value	Stoichiometric value	Experimental value ^a	Stoichiometric value
<i>Cc.</i>	<i>Cc.</i>	<i>Cc.</i>	<i>Cc.</i>	<i>Mg.</i>	<i>Mg.</i>
None	4.07	0.00	0.00	0.00	0.00
0.1	3.85	0.22	0.23	1.93	2.03
0.2	3.61	0.46	0.46	4.03	4.05
0.3	3.40	0.67	0.69	5.88	6.08
0.4	3.14	0.93	0.92	8.16	8.10
0.5	2.90	1.17	1.16	10.26	10.13
0.6	2.65	1.42	1.39	12.45	12.16
0.7	2.44	1.63	1.62	14.30	14.18
0.8	2.22	1.85	1.85	16.22	16.21
0.9	2.00	2.07	2.08	18.15	18.14
1.0	1.76	2.31	2.31	20.26	20.26
1.1	1.52	2.55	2.54	22.36	22.29
1.2	1.30	2.77	2.77	24.29	24.31
1.3	1.12	2.95	3.00	25.87	26.34
1.5	0.75	3.32	3.47	29.12	30.39
1.7	0.55	3.52	3.93	30.87	34.44
1.9	0.42	3.65	4.39	32.01	38.49
2.1	0.30	3.77	4.85	33.06	42.55

^a 1 cc. of the thiosulfate solution was equivalent to 8.77 mg. of maltose anhydride.

DETERMINATION OF MALTOSE IN PRESENCE OF HEAVY WATER. Equal weights of maltose were dissolved in 100 per cent purified heavy water (5) and in redistilled ordinary water and analyzed by the above procedure with the following results, given in cubic centimeters of 0.05 *M* thiosulfate required for the excess iodine in each case:

Reagents alone plus 1 cc. of ordinary water (blank)	4.07, 4.07
Reagents alone plus 1 cc. of 100 per cent heavy water (5) (blank)	4.07, 4.07
1 cc. of a solution of maltose dissolved in ordinary water	2.13, 2.13
1 cc. of a solution of maltose dissolved in 100 per cent heavy water (5)	2.13, 2.12

These data make it evident that the method outlined here may be used for the determination of maltose in the presence of heavy water.

Summary

A rapid and convenient method for the quantitative determination of reducing sugar (maltose) formed in the hydrolysis of starch by amylases is briefly described. It is especially recommended for studies of amylase action in the presence of heavy water.

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Determination of Phosphorus in Stainless Steels

A Rapid Method Using Perchloric Acid

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IN THE course of recent months, the materials testing laboratories of the Tennessee Valley Authority have been called upon to make a large number of analyses of stainless steels. Particular stress was placed upon the rapidity with which the analyses could be made. The analysis in general presented no unusual difficulties, but since time was an important factor, a more rapid method for the determination of phosphorus was sought to replace the one now in general use. The method now used requires the action of hydrochloric-nitric acid mixture to effect solution of the sample, oxidation of phosphides to phosphate, and the subsequent removal of hydrochloric acid, at best a time-consuming operation fraught with many difficulties.

Perchloric acid (60 per cent) was found to be suitable for replacing the above-mentioned acid mixture, thus eliminating the necessity of removal of hydrochloric acid. It is known that perchloric acid interferes neither with the precipitation of ammonium phosphomolybdate nor with its estimation by alkalimetric methods (6). It is shown below that phosphides in steel are completely oxidized to phosphate by the action of hot 60 per cent perchloric acid. The use of weaker concentrations of perchloric acid is not recommended. Lundell advises that from 10 to 15 per cent of the phosphorus may be lost if a 50 per cent acid is used (5).

The speed of the method lies in obviating the necessity of removing chlorides and in circumventing oxidation by nitric acid and potassium permanganate as practiced in the normal phosphorus procedure (4). It is known that perchloric acid may be used for the removal of chlorides, when present, as hydrochloric acid in phosphorus determinations (7), but the power of perchloric acid to oxidize phosphides to phosphate has apparently not been described. The authors' conclusions with regard to the accuracy and the precision of the suggested method are based on the results of repeated analyses of several Bureau of Standards samples and a comparison with the certified values given therewith. The data given below show close agreement with Bureau of Standards phosphorus values.

To show that perchlorates do not interfere with the precipitation of ammonium phosphomolybdate, a series of determinations on pure diammonium phosphate was made in the presence of normal concentrations of perchloric acid. The results (Table III) gave close checks with the calculated theoretical phosphorus content of the salt in each case. In the determination of phosphate in iron ore, Willard has substituted perchloric acid for nitric acid in the procedure for the removal of chlorides after silica dehydration. He re-

ports that the presence of perchloric acid introduces no error (11).

In this laboratory, this method has resulted in more than 50 per cent saving in operator's time in the analysis of stainless steels. Fewer losses by splattering occur and, in general, greater accuracy has been obtained.

While 60 per cent perchloric acid is among the more expensive analytical reagents, the saving in operator's time more than compensates for the additional cost. The cost of the chemicals for this method amounts to approximately 7 cents per determination.

Experimental

REAGENTS. The reagents for this method are essentially those required in the normal determination of phosphorus in steel, plus 60 per cent reagent grade perchloric acid (1).

Procedure

To a 2.00-gram sample placed in a 500-ml. Erlenmeyer flask, add 20 ml. of 60 per cent perchloric acid and warm to effect complete solution. Cover with a funnel, the stem of which has been removed, and boil for 30 minutes or until the chromium is completely oxidized. Here a modified still head, as described by Smith, may be used to advantage (8). The solution should be a deep red to brown color. Cool, dilute to 100 ml., and add ammonium hydroxide (specific gravity 0.90) until a slight precipitate is formed. Approximately 12.5 ml. will be required. Dissolve the brown precipitate by the addition of nitric acid (specific gravity 1.20). Here 20 to 25 ml. will suffice. Add 1 to 5 ml. of 1 to 10 ammonium bisulfite, sufficient to reduce the chromium and vanadium present (ferrous sulfate may be used for this reduction). Boil to remove nitrous oxide fumes and free chlorine (2). Allow the solution to cool slightly, add 50 ml. of ammonium molybdate solution, and agitate for 5 minutes. Allow the precipitate to settle at room temperature for 2 hours or more.

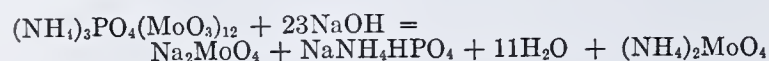
Filter the yellow precipitate and wash from the containing vessel, first with 2 per cent nitric acid five to ten times to remove iron salts, and subsequently with 2 per cent potassium nitrate solution until the filtrate is no longer acid to litmus paper. Place the precipitate with the filter paper in the original precipitation vessel, dilute with about 50 cc. of water, and then add 8 drops of phenolphthalein indicator. Add an excess of standard sodium hydroxide solution and agitate to effect complete solution of the yellow precipitate. Titrate the excess of alkali with standard acid solution.

If the standard solutions are adjusted to 0.149 N, 1 ml. of alkali consumed by the yellow precipitate will be equivalent to 0.01 per cent of phosphorus in the original 2.00-gram sample. The alkali was standardized against Bureau of Standards potassium acid phthalate. The acid was then,

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in turn, standardized against the alkali and the theoretical factor (1 to 23) was used in the titrations according to the reaction (4)



Discussion and Notes on Procedure

The presence of vanadium in quantities up to 0.25 per cent seems to present no difficulty in this method since it appears in the precipitation reaction in the reduced state. If, however, the operator fails to reduce this element, error will be admitted in the form of apparent high phosphorus percentage. Bureau of Standards samples, No. 73 stainless steel, No. 101 18-8 chrome-nickel steel, and No. 30c chrome-vanadium steel, all contain vanadium in appreciable quantities, yet the results in Table I are in keeping with the certified phosphorus values.

The quantity of silicon normally encountered in stainless steels failed to affect the results noticeably when alkalimetric methods were used in the final estimation. Gravimetric procedures, of course, call for the removal of silica before precipitation and this may be readily done when perchloric acid is used for initial solution, since silica appears in its most tractable form when dehydrated with this acid. In fact, silicon may be determined by the Willard and Cake method (12) on the same sample originally weighed for phosphorus.

Smith and Goehler have proved that vacuum-distilled perchloric acid is free from phosphorus (9). Blank determinations of perchloric acid used in these tests confirmed their findings. It is therefore unnecessary to run blank determinations if it is known that the perchloric acid is purified by vacuum distillation.

For plain carbon steels (Tables I and II) this method may also be applied. The authors' conclusions in regard to its use in the analysis of plain carbon steels have been confirmed in parallel tests by Willard and Delp (10). Likewise, high-phosphorus iron may be analyzed. Nothing will be gained, however, by the use of perchloric acid in the analysis of any material which is normally soluble in nitric acid.

An effort was made to eliminate the neutralization of perchloric acid by ammonia and the reacidification with nitric acid by the addition of ammonium nitrate directly to the reaction mixture. The results were not consistently good.

The method seems applicable to phosphorus concentrations over a wide range. Bureau of Standards sample No. 56, brown phosphate rock, was checked by this method and the results were comparable with those obtained by the usual alkalimetric method (3).

The analysis of several Bureau of Standards samples indicates that the accuracy and precision of the method using perchloric acid is good. Table I shows results obtained with the perchloric acid method using acid-alkali titration.

TABLE I. RESULTS WITH PERCHLORIC ACID METHOD

Bureau of Standards Sample	Number of Determinations	Certified Phosphorus Value %	Phosphorus Found		
			Average %	High %	Low %
No. 73 stainless steel	4	0.023	0.023	0.024	0.022
No. 101 18-chromium 8-nickel steel	3	0.011	0.011	0.012	0.010
No. 8d bessemer steel	3	0.099	0.097	0.098	0.096
No. 20c A. O. H. steel	3	0.044	0.042	0.043	0.042
No. 30c chrome-vanadium steel	4	0.019	0.019	0.022	0.018
No. 7c cast iron	3	0.78	0.80	0.80	0.80

Table II gives the results of analyses performed in the same manner as given above, except that the phosphorus is determined finally as in the usual gravimetric method by precipita-

tion as magnesium ammonium phosphate and ignition to the pyrophosphate.

TABLE II. DETERMINATION OF PHOSPHORUS

Bureau of Standards Sample	Number of Determinations	Certified Phosphorus Value %	Phosphorus Found		
			Average %	High %	Low %
No. 8d bessemer steel	3	0.099	0.105	0.108	0.101
No. 20c A. O. H. steel	2	0.044	0.042	0.042	0.041

The results of several aliquots of pure diammonium phosphate are given in Table III. In each case the aliquot was equivalent to 0.235 mg. of phosphorus, a quantity in the same order as those quantities occurring in the Bureau of Standards samples used in this investigation.

TABLE III. RESULTS WITH PURE DIAMMONIUM PHOSPHATE

Sample	Number of Determinations	Phosphorus Present %	Phosphorus Found		
			Average %	High %	Low %
(NH ₄) ₂ HPO ₄	5	0.235	0.232	0.235	0.226

It is likely that this method may be applied to the analysis of phosphor-bronze with considerable savings in operator's time. Work on such a method is now in progress in this laboratory.

Summary

The phosphorus content of difficultly soluble steels, such as stainless steels, may be quickly determined by dissolving and subsequently boiling the sample in 60 per cent perchloric acid before subjecting it to normal analytical procedures. Perchlorates do not interfere with the determinations of phosphorus either in volumetric or gravimetric methods.

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Bituminous Plastics

Determination of Flow Properties

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AMONG bituminous technologists the terms "plastic" and "plastic cement" are usually reserved for three-phase compounds made up of bitumen, solvent, and filler. In most cases the latter is composed of fibrous material, either alone or in combination with a granular mineral powder. However, in the discussion to follow, a bituminous plastic will be considered as any asphaltic material which shows a definite deviation from viscous flow—i. e., exhibits a curvilinear relationship between flow and shearing stress. These substances may or may not possess an apparent yield value, but they all exhibit, in varying degrees, elasticity, thixotropy, and comparatively great resistance to deformation. The more highly filled materials frequently show the phenomenon of dilatancy (20).

Karrer (12) in a discussion of plasticity mentions the prevailing tendency to classify materials by the manner in which they may be plasticized. If such a classification is employed, the bituminous materials to be discussed must be described as thermoplastics because they are workable and moldable when hot. Cameron and Lineberry (4) suggested, however, that the term "plasticity" be applied only to dispersed systems in which at least one component is a film-forming liquid. This definition describes most bituminous plastics.

Methods for Studying Flow Properties

Several distinctly different methods for obtaining information concerning the flow properties of bituminous materials have been used recently in this laboratory. Although some of the methods were not thoroughly explored, valuable information concerning the nature of the flow of asphaltic materials was obtained by the various approaches.

A parallel-plate plastometer similar to that described by Peek (17) was employed to study the flow properties of viscous bitumens filled with large amounts of pulverized minerals. In this machine a constant load is applied to a small briquet of the plastic material, and the rate of movement in the sample is followed by means of an Ames dial. The graphical method of treating the data advocated by Peek was tedious if a large number of mixtures was to be investigated. For some purposes the more rapid method of treatment proposed by Manning (14) should be satisfactory.

A mixture made up of 39 per cent by volume of pulverized slate and 61 per cent by volume of a soft bitumen (48 seconds coat at 150° F. or 65.6° C.) was cast in the form of a cylinder 1.540 cm. in diameter and 0.793 cm. high. This sample was placed in the parallel-plate plastometer at 25° C. and subjected to a load of 11,500 grams for 336 hours (1,209,600 seconds). By analyzing the data obtained during the first two or three hours by the graphical method mentioned, a yield value of approximately 360,000 dynes per sq. cm. was obtained for this slate-bitumen mixture. However, as shown by the data in Table I, the mixture was still flowing after 336 hours had elapsed and when the sample was 45 per cent of

The complicated flow properties of bituminous plastics probably cannot be satisfactorily evaluated by any single method discussed. On account of the number of variables encountered and the varying degrees in which each property may appear, absolute values will be difficult or impossible to attain. However, this fact should not discourage the investigator from employing any of the methods of rheology, since only by means of such approaches can a clear understanding of the behavior of bituminous plastics under service conditions be acquired.

its original height. These results indicate that the yield value ascribed to many bituminous materials may be a fictitious value obtained through the use of insufficient data.

Careful measurement with this instrument indicated that even highly filled compounds, containing as little as 10 or 12 per cent bitumen, do not possess a true yield value. Nevertheless, valuable comparisons of various mixtures may be obtained by calculating an apparent yield value for each compound from the deformations occurring during the course

of one or two hours in the plastometer.

The parallel-plate plastometer in a modified form was also used to obtain information concerning the elastic properties of mixtures of sand, mineral powder, and bitumen, in which the latter is present only to the extent of 10 per cent by weight. A rather large force was applied to the briquet of plastic material for a length of time sufficient to cause complete elastic compression without appreciable permanent deformation. The load was then carefully but quickly raised and the instantaneous recovery in sample height noted. After several minutes the upper plate of the plastometer was again lowered

TABLE I. FLOW OF SLATE-BITUMEN MIXTURE IN PARALLEL-PLATE PLASTOMETER

Time ^a Sec.	Height of Sample Cm.	Time ^a Sec.	Height of Sample Cm.	Time ^a Sec.	Height of Sample Cm.
0	0.7930	80	0.4022	258,000	0.3622
5	0.4670	210	0.3862	600,000	0.3587
10	0.4480	600	0.3782	885,600	0.3575
15	0.4385	2400	0.3751	950,000	0.3567
20	0.4310	21,800	0.3719	1,209,600	0.3560
40	0.4168				

^a In order to conserve space, all of the intermediate values are not recorded.

into contact with the sample, and the final recovered height was recorded. This procedure was repeated several times, and the average value thus obtained was used in calculating the modulus of elasticity of the paving mixture. The testing loads were applied in decreasing order of magnitude. Moduli of elasticity, for two-sheet asphalt paving mixtures, determined by this method are as follows; the bitumen used in preparing these mixtures was a batch steam-processed oil asphalt of 50 penetration at 25° C., 100 grams, 5 seconds:

Bitumen —Per cent by weight—	Limestone Dust Sand		Temp. ° C.	Elastic Modulus	
				Dynes/sq. cm.	Lb./sq. in.
12	10	78	24.7	5.9×10^8	8.5×10^3
9	10	81	25.0	6.5×10^8	9.5×10^3

In addition to the parallel-plate plastometer, a Baldwin-Southwark compression testing machine was used to obtain preliminary data concerning the flow of asphalt paving mixtures under compression. The moduli of elasticity were determined on a variety of paving mixtures, and values were

obtained for the yield point, ultimate strength, and mobility. At the present time the amount of data available using this machine is limited, and all its possibilities have not been fully explored.

The alternating stress method described by Bingham and Stephens (3), which utilizes a cylinder of the material cast in a glass tube, was used to investigate the flow characteristics of viscous bitumens (18, 21) as well as some air-blown asphalts and a large number of rather soft, mineral-filled compounds which possess only moderate plastic properties. Apparent viscosities at 60° C. and at different shearing stresses are given in the following table for a mineral-filled air-blown bitumen possessing a penetration of 15 at 25° C., 100 grams, 5 seconds:

Shearing Stress Dynes/sq. cm.	Apparent Viscosity at 60° C. Poises $\times 10^{-6}$	Shearing Stress Dynes/sq. cm.	Apparent Viscosity at 60° C. Poises $\times 10^{-6}$
104,200 (out)	9.30	62,240 (out)	6.44
104,200 (in)	6.28	62,240 (in)	6.41
91,600 (out)	4.75	52,750 (out)	7.99
91,600 (in)	4.58	52,750 (in)	7.77

These data give considerable information concerning the flow properties of the compound. Structure within the bituminous material is rapidly destroyed by the mechanical working to which the sample is subjected. This explains the large decrease in apparent viscosity which occurs between the first and second "out" determinations—the material is thixotropic. Presence of elasticity in the sample is evident from the fact that the "out" values are always higher than the "in" values. Finally, the increase in viscosity with decreasing shearing stress indicates that the material is not purely viscous. If the determinations had been made at a lower temperature, all of the above effects would have been amplified.

The consistencies of bituminous materials increase with age, rapidly at first and then more slowly, as a longer time elapses since the material was in a molten condition. This increase in consistency is not due to the loss of volatile constituents because careful remelting and cooling will effect a return to the original value. Time-hardening in bituminous materials, which is being studied at present by means of the falling coaxial cylinder type of viscometer (19), appears to be due to the development of some type of structure within the material. Seven falling coaxial cylinder viscometers were filled with a soft air-blown bitumen (90 penetration at 25° C., 100 grams, 5 seconds). One sample was brought to 25° C. and a determination was made 4 hours after pouring. The remaining loaded viscometers were placed in a constant-temperature cabinet maintained at 25° C. and left undisturbed at that temperature until removed for testing. The times and experimentally determined viscosities for the air-blown asphalt are as follows; a shearing stress of 17,000 dynes per sq. cm. was used for each determination:

Time Hours	Viscosity at 25° C. Poises $\times 10^{-6}$	Time Hours	Viscosity at 25° C. Poises $\times 10^{-6}$
4	12.3	171	21.7
25	15.1	507	24.9
52	16.3	700	31.4
100	18.8		

A similar set of experiments was performed using six viscometers filled with an asphalt (55 penetration at 25° C., 100 grams, 5 seconds) produced from Mexican petroleum in a vacuum still. The data for this vacuum-refined asphalt are as follows:

Time Hours	Viscosity at 25° C. Poises $\times 10^{-6}$	Time Hours	Viscosity at 25° C. Poises $\times 10^{-6}$
4	5.13	171	5.94
24	5.51	507	6.52
72	5.71	1012	6.71

Steam- and vacuum-refined asphalt do not show as rapid an increase of viscosity with time as do the air-blown bitumens. The structure which probably accounts for this time-hardening can be destroyed by heating above the softening point but begins to return immediately upon cooling. Mechanical working is also capable of eliminating the hardening influence of time to some extent.

The application of the falling coaxial cylinder viscometer to the study of plastic materials is limited in about the same way as the alternating stress method, in that the material cannot be sheared continuously for any appreciable length of time. Also, the rates of shear cannot be varied over a wide range. These criticisms cannot be raised against the rotating cylinder type of viscometer (7, 16) since by the use of such an instrument it may be possible to break down the structure to a greater degree than is possible in either the tube or falling cylinder viscometer, thus giving values for the consistencies of bituminous plastics in the worked condition. However, the practical value of any bituminous plastic may bear very little relationship to its consistency in the worked state, since the material usually serves its purpose in the unworked condition.

Plasticity of Filled Bitumens

Green and Haslam (9) concluded, from a study of the relationship between yield value and particle size, that plasticity was influenced by the interfacial area and number of points of contact of the dispersed phase per unit cross-sectional area. These effects and relationships have been found to hold in general for bituminous plastics. Also, the amount of elasticity, thixotropy, and dilatancy, as well as the plasticity, exhibited by the system will depend on the characteristics of the solid and liquid, and the ratio of the volumes of the two phases. Some bituminous plastics, which contain only a small amount of dispersed phase, may acquire the characteristics of a viscous liquid after being subjected to prolonged working. In those with appreciable amounts of filler the structure cannot be completely eliminated, and thus their flow properties are anomalous under all conditions of test.

When a viscous bitumen is filled with a mineral powder the consistency increases gradually until a concentration is reached, depending on the characteristics of the bitumen and the powder, where nonviscous flow begins to appear. The degree of "plasticity," elasticity, and in fact all phenomena dependent upon structure within the material becomes more conspicuous as the concentration of filler increases. A number of measurements are given below to illustrate the appearance of plastic or nonviscous properties with an increase in the amount of dispersed phase in a bituminous mixture. The compounds employed were prepared using various proportions of an asphalt produced by the vacuum distillation of California petroleum and a finely ground pumice. The asphalt had a penetration of 55 at 25° C. (77° F.), 100 grams 5 seconds, and a Ball and Ring softening point of 47° C. (116.5° F.). Measurements made by the Bingham-Stephens alternating stress method at 25° C. gave the same viscosity values for different shearing stresses, and thus the bitumen was assumed to be a viscous liquid. Viscosity data on this vacuum-refined asphalt are as follows:

Shearing Stress Dynes/sq. cm.	Viscosity at 25° C. Poises $\times 10^{-6}$	Shearing Stress Dynes/sq. cm.	Viscosity at 25° C. Poises $\times 10^{-6}$
33,382	3.17	22,057	3.09
33,086	3.14	18,132	3.13
28,677	3.13	15,437	3.09
25,484	3.03		

Mixtures were prepared using 90, 80, and 70 per cent by volume of this bitumen combined with 10, 20, and 30 per cent

by volume, respectively, of pulverized pumice. The consistencies of the mixtures were measured at 25° C. by the method used for the bitumen. Table II gives the data obtained.

TABLE II. VISCOSITY DATA ON BITUMEN-PUMICE MIXTURES

90% Bitumen 10% Pumice		80% Bitumen 20% Pumice		70% Bitumen 30% Pumice	
Shearing stress	Apparent viscosity at 25° C.	Shearing stress	Apparent viscosity at 25° C.	Shearing stress	Apparent viscosity at 25° C.
Sq. cm.	Poises × 10 ⁻⁶	Dynes/sq. cm.	Poises × 10 ⁻⁶	Dynes/sq. cm.	Poises × 10 ⁻⁵
52,305	4.77	66,490	10.11	64,270	29.62
51,791	4.75	66,490	9.16	64,147	24.72
46,358	4.79	59,480	8.77	63,993	22.80
41,441	4.69	52,784	8.66	55,763	22.08
36,585	4.72	46,088	8.36	47,193	21.15
31,564	4.80	39,967	8.65	42,076	20.13
26,214	4.86	33,794	8.40	34,278	19.40

The data indicate that the mortar containing 10 per cent by volume of pumice was essentially a viscous liquid. However, when 20 per cent of this particular filler was present, a small amount of structure appeared and had to be worked out of the sample before even approximately constant values or viscosities at different shearing stresses were obtained; thus, these values illustrate the type of data obtained on materials which are thixotropic. When the concentration of pumice was increased to 30 per cent by volume, the deviations from viscous flow became very definite and even prolonged working in the viscometer did not completely eliminate the effects due to structure in the mass. From these facts it is evident that appreciable amounts of dispersed material must be added to viscous bitumens in order to create sufficient structure within the system to give even mild plastic properties.

Paving Mixtures

Using the definitions given at the beginning of this paper, all asphalt paving mixtures may be considered as plastics. According to Horsfield (10), the resistance of an asphaltic paving mixture to deformation depends on the interlocking and friction developed between the particles of mineral aggregate and to the viscous resistance of the bitumen. Thus, a close-packed aggregate is necessary in order to obtain a high frictional resistance. "The asphalt mixture at first has no internal frictional resistance and is a liquid, but by the end of the test its structure has so altered in the stressed state that the bulk of the resistance is frictional and the remainder viscous. In other words, it has become a plastic solid and this change has been effected solely by stressing the mixture." Horsfield thus describes what is probably a manifestation of the phenomenon of dilatancy.

Of the numerous methods devised for estimating the stability of asphalt paving mixtures, one of the most widely used is that described by Hubbard and Field (11). In this test a cylindrical briquet 2 inches (5 cm.) in diameter and 1/2 inch (2.5 cm.) thick is formed from the paving mixture in a standard type of mold under a specified pressure. If hot, the briquet is allowed to cool and age for a short time; then after warming to 60° C. (approximately the maximum temperature of a pavement under a summer sun), it is placed in a testing mold. The test consists in measuring the maximum load required to force the mixture through a circular orifice 1/4 inch (4.4 cm.) in diameter. This load is recorded as the stability value of the mixture.

The Hubbard-Field test measures the initial resistance to shear and not the mobility of the paving mixture. This initial resistance to deformation depends to a great extent upon the closeness of packing of the mineral aggregate; thus, the degree to which the sample is compressed before the test is made becomes important.

Milburn (15), Emmons and Anderton (8), Wilson (2),

Chatillon (5), and Skidmore (1) have devised methods and apparatus for estimating the stability, plasticity, and resistance to shear of bituminous paving materials. Reference should be made to the original descriptions for details concerning the construction of the various instruments and the preparation and testing of the samples. Of these methods, that of Skidmore which measures the resistance to shear of the mixture is the most widely used.

Roofing Asphalts

Roofing asphalts, which are usually prepared with air-blown bitumen, are another important class of bituminous plastics. Resistance to disintegration by exposure to sun, air, and water, elasticity at low temperatures, and absence of deformation at summer temperatures are the prime requisites of a plastic to be used in the production of roofing materials. Fiber-filled plastic cements are used extensively in repairing bituminous and metal roofs, and in constructing flashings, sealing laps, and closing or filling the valleys around vents and other objects. Certain types may also be used under heavy roofing tiles.

An apparatus based on the principle of the falling ball and falling cylinder viscometers and used for measuring the "worked" consistencies of roofing putties and fibrous roof coatings prior to the evaporation of the solvent has been developed by Clarvoe (6). Either a ball or a cylinder attached to a rod is permitted to sink through the plastic mass under constant load, and the rate of fall is taken as a measure of the consistency. The cylinder is used with heavy putties and the ball with materials which are so thin that they are usually applied with a brush.

Flooring Materials

Highly filled asphalts are moldable into tiles, slabs, or planks which may be laid as a floor covering over some strong but less flexible or elastic foundation. In mastic floors the bituminous plastic is placed over the foundation in a continuous sheet. The resiliency of such floors makes them desirable where workers are on their feet all day.

McBurney (13) has developed and described a portable instrument for measuring the ease of indentation of asphaltic tile and other materials by means of a metal sphere. His method of test should be given careful consideration because it can be applied to plastic materials *in situ*, whereas most other methods treat them in the form of a small sample and usually in a worked condition. The evaluation of most bituminous materials (e. g., paving mixtures) after they have been put into position would be valuable since there is always present the danger of drawing false conclusions concerning the behavior of a material under actual conditions of use from tests made in the laboratory under entirely different conditions and environment. McBurney has developed an empirical formula which relates the depth of indentation to the load and diameter of sphere, and to the time during which the loaded sphere acts upon the material.

Acknowledgment

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Preparation and Storage of Standard Chromous Sulfate Solutions

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THE preparation and storage of standard chromous reducing solutions are of special importance, for this reagent is the most powerful of any of the well-known reducing agents which can be used as an aqueous solution. The change from Cr^{++} to Cr^{+++} has a molal oxidation-reduction potential of -0.41 volt (5). Its reaction with the oxygen of the air is extremely rapid. Hence, like titanous solutions, the chromous reagent must be protected from the atmosphere at all times. The lack of an entirely satisfactory method of preparation and the difficulty involved in excluding the air from the reagent have greatly curtailed its use. The present work describes both a simple efficient method of

preparing the chromous sulfate reagent and an improved method of protecting it from the atmosphere.

Thornton and Sadusk (9) report preparation of the chromous reagent—by a reduction of an acid solution of potassium dichromate with zinc amalgam in a Jones reductor. A $0.067 N$ solution of chromous sulfate was obtained by them which was not over $0.18 N$ in sulfuric acid, representing a 67 per cent yield. The rate of reduction was 40 ml. of solution per minute. Carbon dioxide was used to exclude the air during the preparation. Apparently, the reagent was stored under hydrogen from a Kipp generator (10).

When this method was used by the authors, the concentrations of the resulting chromous solutions varied so greatly that it was necessary to start with two or three times the theoretical requirement of dichromate to insure a given concentration of the reagent. During certain experiments, the rate of flow of the solution through the Jones reductor was reduced to a few milliliters per minute by the buoyant effect of the hydrogen resulting from the action of the acid on the zinc. This effect was dependent on the concentration of the acid and the extent to which the zinc had been amalgamated. A more complete amalgamation of the zinc eliminated the hydrogen but reduced the yield. A considerable concentration of acid was required to enable the zinc to reduce the potassium dichromate satisfactorily. Because of the reaction of the acid with the zinc, there was always an uncertainty as to the acidity of the resulting solution. Solutions of low acidity could not be prepared by this method. The quantity of nonessential ions introduced into the solutions was large.

The use of violet chrome alum solutions, in place of the strongly acid potassium dichromate solutions in the preparation of the chromous reagent, has been found to eliminate the acid difficulties and to reduce the unavoidable ions in the final solutions by at least 40 per cent. In addition to this, yields of from 90 to 100 per cent of the chromium in the chromous form were obtained at from two to five times the rate of reduction used by Thornton and Sadusk (9).

A list of references on the subject of the preparation and use of chromous solutions in analysis is given by Brennecke (2).

Influence of Complex Chromic Salts

The fact that chromic salts exist in solution in both violet and green modifications is of im-

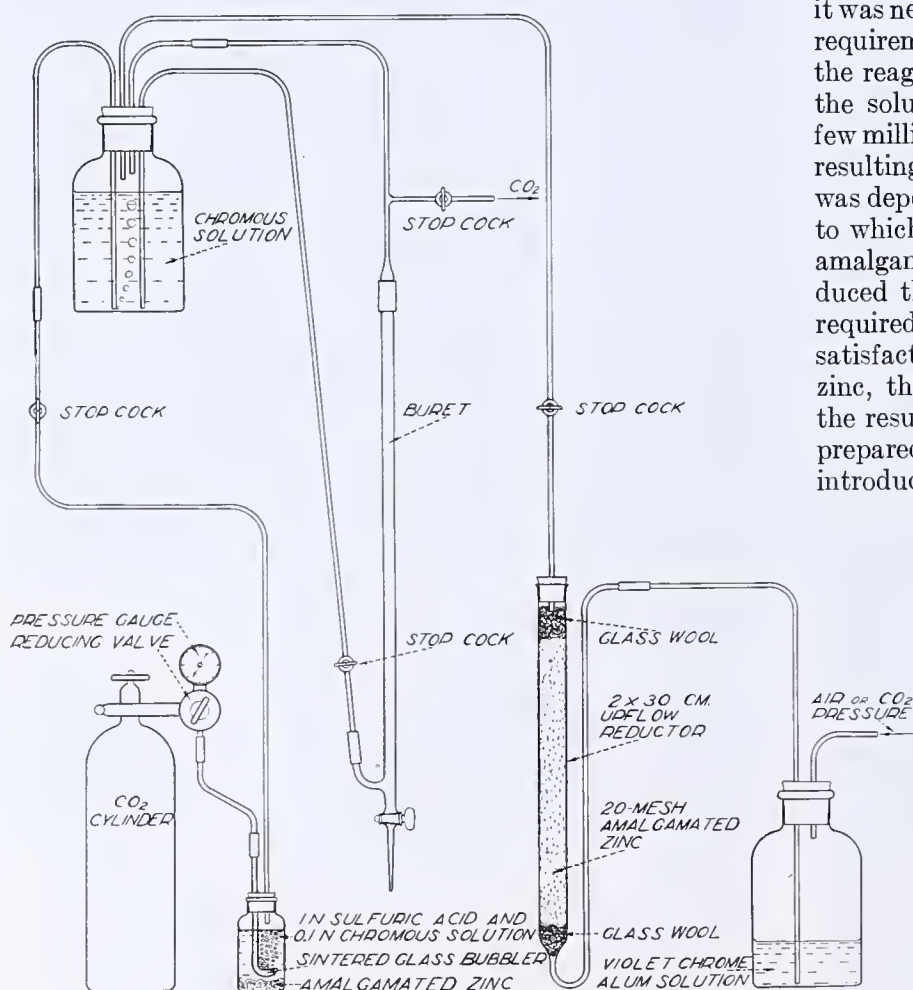


FIGURE 1. DIAGRAM OF APPARATUS

portance in this work. At room temperatures these forms are at equilibrium and when the equilibrium is disturbed it is adjusted rather slowly. The authors found that the violet solutions were more rapidly reduced than the green ones. Three factors which were observed to favor the rapid reduction are also known to promote the formation of the violet complex in the solution. A chrome alum solution that has been freshly prepared, that is made up in dilute sulfuric acid solution, and that is held at room temperature or below, is violet in color and rapidly reduced by the zinc amalgam in a Jones reductor. If the solution is allowed to stand, if acid is not added, or if the solution is heated, there is a shift to the green color and the rate of reduction is less. The effect of the acid on the color has been shown by Orlova and Petin (8). The fact that higher temperatures and aging of the solution tend to favor the green form is proved by the work of Montemartini and Vernazza (7).

The violet color in chrome alum solutions is thought to be due to complex groups in which six water molecules are coordinated with chromium as in $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$, while the change to the green color involves the replacement of two or more of the water molecules in the complex with sulfate ion. $[\text{Cr}(\text{H}_2\text{O})_4\text{SO}_4]^+$ represents one of several possible complex ions of the green type. This situation is complicated by the fact that these groups are hydrolyzed in the solution and by the fact that they exist as condensed aggregates. Graham (4) gives a comprehensive bibliography of this subject.

Experimental Work

The amalgamated zinc was prepared by stirring 240 grams of 20-mesh c. p. zinc in 100 ml. of 3 *N* hydrochloric acid for 30 seconds. Then 100 ml. of 0.013 *M* mercuric chloride solution (5 ml. of a saturated solution at 25° C. diluted to 100 ml.) were added to the zinc acid mixture. Soon after the addition of the mercuric chloride the evolution of hydrogen practically ceased. The stirring was continued for 3 minutes longer, after which the amalgamated zinc was washed thoroughly with distilled water by decantation.

The reductor shown in Figure 1 was then filled with the amalgamated zinc. In this device, the customary Jones reductor was modified so that air pressure was used in place of hydrostatic pressure to force the solution through the reductor. Moreover, the usual direction of flow through the reductor was reversed, causing the liquid to flow up through the amalgamated zinc. The use of air pressure permitted the investigation of much higher rates of flow. The reversal of the direction of flow took advantage of the buoyancy of any hydrogen liberated in the reductor. The hydrogen aided the flow of the liquid instead of hindering it, as is the case in the usual form of reductor.

The drawing (Figure 1) of the arrangement used in preparing the chromous reagent, and in protecting it from the air during the determination of its concentration, requires little explanation. Before starting the preparation of the chromous reagent, the air was flushed from the system by a stream of carbon dioxide from the cylinder. The gases escaped through the outlet above the buret. While the stream of gas was maintained, the stopcock above the reductor was opened and the chrome alum solution was forced through the amalgamated zinc. When sufficient chromous reagent had been prepared, the line from the reductor was cut off, and the chromous solution was thoroughly agitated by a stream of carbon dioxide bubbles. After about 15 minutes of such agitation the outlet above the buret was closed and the reagent was ready for titration.

The air was effectively excluded from the stored reagent by means of a small pressure of carbon dioxide. The use of the pressure reducing valve and gage made it possible to reduce the high pressure from the liquid carbon dioxide to the fairly constant low pressure required to exclude the oxygen of the air from the reagent. This low pressure was comparable to that obtained from a Kipp generator. The pressure could be maintained without the escape of gas and without the building up of pressure in the system. This method was far more satisfactory than the use of a Kipp generator, such as has been recommended by Zintl and Rienäcker (11) and

Thornton and Wood (10). Moreover, the valve and gage, which cost about \$7, were no more expensive than the Kipp generator which they displaced. The cylinder of carbon dioxide involves no extra expense, since in using such a reducing agent a cylinder of inert gas is usually required for flushing out the titration beaker. The usual arrangements for anaerobic work have been modified to meet the requirements of repeated preparation and testing of the concentration of the reagent. Readers desiring details of methods for the storage and use of such reagents are referred to the authors mentioned above (10, 11), and particularly to Crowell and Baumbach (3). It would seem that wherever standard solutions are to be protected from the oxygen of the air by the pressure of an inert gas, the use of the pressure reducing valve and cylinder of gas would be desirable.

Although liquid carbon dioxide is usually free from oxygen or other impurities which might oxidize the chromous ion, the precaution was taken of purifying the gas used. As shown in Figure 1, the carbon dioxide entered the wash solution through a Jena sintered-glass distribution tube. This insured a thorough mixing of the gas with the chromous sulfate-sulfuric acid solution which is capable of absorbing oxygen very rapidly. The amalgamated zinc, in the bottom of the bottle, served to regenerate any chromous ion which may have been oxidized.

Because it has been reported that hydrogen may be liberated from acid solutions by the chromous ions, the authors considered this possibility carefully and found no evidence of such a reaction under the experimental conditions of this work. There can be no doubt as to the stability of chromous sulfate-sulfuric acid solutions with respect to this reaction, in view of the fact that Thornton and Sadusk (9) and Crowell and Baumbach (3) reported no appreciable change in the titer of such solutions over a period of a month. Asmanoff (1) found that chromous sulfate did not liberate hydrogen even from 10 *N* sulfuric acid, but that it did react slowly with 4 *N* hydrochloric acid, and that ammonium salts and platinum catalyzed the liberation of hydrogen from sulfuric acid by chromous sulfate. That no change of titer was observed in this work with the solutions containing hydrochloric acid may be explained by the fact that the concentration of the hydrochloric acid never exceeded 0.1 *N* and that the period of storage was never more than a few hours at the most.

The titer of the chromous reagent was determined by siphoning the solution, under carbon dioxide pressure, into the buret from which it was delivered below the surface of an excess of standard potassium triiodide solution. After dilution and acidification, the excess of triiodide was determined by titration with sodium thiosulfate solution. Each yield in the tables represents an average of two or more closely agreeing duplicate determinations on each sample prepared. Any possible effect of oxygen dissolved in the potassium triiodide solution was neglected. The percentage yield was based on the assumption that the c. p. chrome alum was indeed pure.

The authors did not attempt to determine why 100 per cent yields of the chromous reagent were not regularly obtained when the recommended conditions for the preparation were used. Since Lundell and Knowles (6) have already shown that chromium solutions can be quantitatively reduced by zinc amalgam in a Jones reductor, it seems sufficient to state that the values reported are strictly comparable with each other.

Experimental Results

The experiments of Table I indicate that with an efficient zinc amalgam one may force the solution through the reductor at any convenient rate and obtain satisfactory yields of the chromous reagent. The high rate of 200 ml. per minute,

used in experiment 39S, is about as rapid as it is practicable to force a liquid through such an apparatus. The apparent decrease in yields with the increase in rate, brought out by comparing experiments 21B through 25B, has not been observed in other cases. It might be explained by a decrease in the efficiency of the amalgam, a point discussed later.

TABLE I. RELATION BETWEEN RATE OF FLOW THROUGH REDUCTOR AND YIELD OF Cr^{++}

Expt. No.	Acid	(Concentration of violet Cr^{+++} , 0.1M)			Yield of Cr^{++}
		Age of Cr^{+++} Solution Hours	Rate of Reduction Ml./min.		
21B	0.01 N HCl	0.5	40		100
22B	0.01 N HCl	0.5	40		99
24B	0.01 N HCl	0.5	150		93
25B	0.01 N HCl	0.5	150		91
37S	0.1 N H_2SO_4	2	50		97
40S	0.1 N H_2SO_4	19	120		96
38S	0.1 N H_2SO_4	2.25	135		98
39S	0.1 N H_2SO_4	0.5	200		97

TABLE II. EFFECT OF VARIATIONS IN ACID AND Cr^{+++} CONCENTRATIONS ON YIELD OF Cr^{++}

Expt. No.	Acid	Concn. of Violet Cr^{+++}	Age of Cr^{+++} Solution	Rate of Reduction	Yield of Cr^{++}
		M	Hours	Ml./min.	%
13S	None	0.01	0.5	50	90
41S	None	0.01	0.5	140	92
39S	0.1 N H_2SO_4	0.1	0.5	200	97
22B	0.01 N HCl	0.1	0.5	80	99
28S	0.1 N H_2SO_4	0.4	0.75	17	96

TABLE III. EFFECT OF AGE OF SOLUTION, WITH AND WITHOUT ACID, ON YIELD OF Cr^{++}

Expt. No.	Acid	Concn. of Violet Cr^{+++}	Age of Cr^{+++} Solution	Rate of Reduction	Yield of Cr^{++}
		M	Hours	Ml./min.	%
28S	0.1 N H_2SO_4	0.4	0.75	17	96
29S	0.1 N H_2SO_4	0.4	27	17	93
38S	0.1 N H_2SO_4	0.1	2.25	135	98
40S	0.1 N H_2SO_4	0.1	19	120	96
41S	None	0.01	0.5	140	92
43S	None	0.01	4	100	84
44S	None	0.01	4.5	150	72

Table II offers evidence that the yield is less where no acid has been added to the chrome alum solution, that satisfactory yields can be obtained with either sulfuric or hydrochloric acid, that a change in concentration of the acid from 0.01 N to 0.1 N does not change the yield materially, and that variations in the Cr^{+++} concentration of the chrome alum solution up to 0.4 M Cr^{+++} do not alter the yield greatly. Though the yield with hydrochloric acid is as good as with sulfuric acid, the hydrochloric acid solutions are known to be less stable.

Experiments 41S, 43S, and 44S show that the longer a chrome alum solution stands, the lower the yield of chromous ion obtained upon reduction. When acid was added to the chrome alum solutions, this reduction in yield with age was

much less. The explanation lies in the fact that the violet chromium complex gradually changed to the more slowly reduced green complex. The shift from the violet to the green form was retarded by the presence of acid, hence the age of the solution was only a small factor where acid had been added.

A solution made from green chromic sulfate crystals was 89 per cent reduced at a rate of 20 ml. per minute and only 44 per cent reduced at a rate of 120 ml. per minute. Similar reductions in yield, in cases where the chrome alum solution had been changed to green by heating, have shown that the rate of reduction is a factor to be considered where the green form is being reduced.

Certain preparations of zinc amalgam, which at first were entirely satisfactory, suffered a loss of efficiency that could not be explained. An example of such an amalgam is found in one preparation which, after having previously been satisfactory, so decreased in efficiency that a chromous yield of only 64 per cent was obtained. By replacing this amalgam with a fresh preparation and keeping all other factors constant, the yield was returned to nearly 100 per cent. This difficulty of low efficiency on the part of the zinc amalgam was met only where the amalgamated zinc had been used and stored under water for a period of not less than several days.

Conclusions

Certain difficulties arising in the use of the Thornton and Sadusk method of preparing standard chromous sulfate solutions have been pointed out. A method of eliminating these difficulties by the use of violet chrome alum solutions in place of potassium dichromate solutions has been given. A study of the factors involved in the preparation has shown that those things which tend to change the violet complex in the alum solution to the green complex, also tend to reduce the yield of the desired reagent. An improved method of protecting the reagent from the oxygen of the air has been described.

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Accelerated Method for Determining Wear Caused by Abrasion

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DETERMINATION of the effect of wear on a given surface over a period of time is a problem similar in many ways to estimating the effect of aging or of weathering on a product. Choice must be made between observing the material actually in use over an extended period of time or of devising a method whereby the action can be accelerated so as to obtain substantially the same effect in a shorter period of time. An accelerated method is preferable and in many cases essential. The usual uncertainty then arises as to how well the artificial conditions imposed correspond to the actual conditions of use.

In starting accelerated wearing tests on flooring materials several years ago, the apparatus that had already been proposed for such a purpose seemed to have a number of disadvantages. In an effort to make the determination correspond more closely to conditions of normal use, a different type of apparatus was set up and the problem approached from a different viewpoint. The apparatus so developed was found later to apply to the study of abrasion on other types of surfaces also. With simple modifications it is believed applicable to shoe leather, the enamel of compacts, linoleum finishes, and other articles receiving frictional wear. The illustrations given are of three typical applications. Similar equipment is known to be in use in industry but no details of design have been published so far as the authors know. It is therefore given as a method which may be found applicable to diverse problems and which is believed to have advantages over the methods already in print.

Of the various methods for determining hardness, only a few measure the type of abrasive action occurring on floors. The Dorry apparatus (6) for testing road materials measures the hardness of a cylindrical sample by abrading it against a steel disk with crushed quartz under a weight of 1250 grams. The duration of the test is for 1000 revolutions of the disk and the results are expressed in terms of hardness where hardness equals 10 minus one-third the loss in weight of the sample in grams. This apparatus has been modified (7) for application with specimens cut from flooring.

Another apparatus, rather similar in principle, but designed particularly for application to flooring, was developed by Kessler (5). In this method, three specimens of the material are abraded against a disk which revolves at 45 r. p. m. A weight of 2000 grams is applied on each specimen and No. 60 artificial aluminum oxide is fed constantly onto the disk as the abrasive. The disk is rotated for 5 minutes and the specimens are weighed in terms of hardness where hardness equals the reciprocal of the loss in volume times a factor. Correlation with service measurements is only fair, but is believed adequate to permit prediction of service wear.

Still another method designed especially to test flooring is that used by the Dow Chemical Company (1) on magnesia cement composition flooring. In this case the essential feature of

Equipment was designed to measure the comparative rate of wear of travertine and an artificial travertine flooring. A silicon carbide block fastened to a reciprocating arm was loaded to a weight of 3000 grams and operated at 30 cycles per minute. Observation shows that after the surface skin is removed from the stone a steady rate of wear is obtained with the particles of fine dust from the stone as the actual wearing agent. The silicon carbide block does not contact the stone. By replacement of the block with a blackboard eraser liberally supplied with chalk the equipment was used for measurement of the rate of wear of a glass blackboard. A miniature machine operating on the same principle was designed and used for comparison of efficiency of tooth pastes in removal of mucin plaques. The equipment appears to be of rather general applicability.

the apparatus is a horizontal blade mounted on a vertical shaft so that the blade revolves just above the sample, pushing six steel cubes around and around over its surface. At the same time silica stucco sand is fed onto the surface of the sample. The abrasive is changed three times during the wearing operation, which is ordinarily for 6000 revolutions of the blade. The results are expressed in terms of the depth of wear obtained as measured by a micrometer mounted in a movable block on a bridge.

Other apparatus has more general application but is based on the same principle of exerting abrasion by revolving the abrading element against the sample. One design (3) consists of an upright leather wheel which rolls with constant slippage on a path of test samples mounted on a horizontal revolving disk. Sand is fed as the abrasive. Another (9) measures wear of leather, tires, etc., against a rotating abrading member in terms of loss of material per unit of abrading powder. Another (2), which has been made the subject of a patent, rotates blocks of the materials to be com-

pared under predetermined pressure around a raceway constructed of the desired abrading agent.

There seemed to be two disadvantages common to all these methods. With respect to flooring particularly, observation shows that the wear that occurs very seldom results from rotary motion of an abrading surface. The tread of feet on a floor or stairway in general produces reciprocating motion. With respect to any surface, the abrasive action occurring naturally will only in rare cases be as harsh as that imposed in these accelerated tests. There may be other fundamental differences between the abrasives as well. Undoubtedly the wear on flooring varies as to the nature of the materials causing it. In the extreme case it is partially due to sharp particles. In the normal case examination shows that it is caused by particles of the material itself or of very fine dirt, which, in most cases, are neither sharp nor hard. In setting up a different type of abrasive measurement apparatus, therefore, two specifications were established: (1) that the motion of the abrading element should be in a straight line rather than circular; and (2) that the abrasive action used should correspond as closely as possible to that which would cause the normal wear when the material being studied was in use and therefore consist of only fine, relatively nonabrasive particles such as those derived from the material under test. For general applicability it must be possible to vary the abrasive used.

The use of fine particles of the material under test as the abrasive, in place of other miscellaneous dirt, is believed to introduce no serious variable so long as the material under test is of a fine-grained structure. It does not seem to be an unreasonable extension of Kessler's work (5) to assume that, if the use of coarse abrasive correlates with service results, the correlation with service will be as good or better when fine abrasive is used. Further there is nothing inherent in the

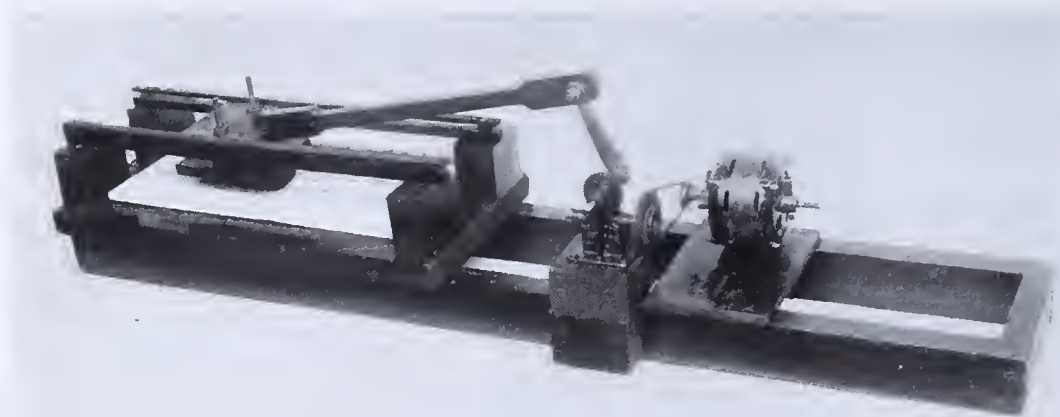


FIGURE 1. APPARATUS USED ON FLOORING

equipment which prevents the use of sharp particles such as silica sand if extreme conditions are to be measured. The equipment is, however, primarily for measurement of normal rather than for abnormal wear.

Naturally, when the second specification is adopted, the duration of the test period must be considerably greater than Kessler's 5-minute period, in order to obtain an appreciable effect. However, the action is still an accelerated one, since the motion can be made continuous as contrasted with actual use, where the impact of an abrading element, such as a footstep on flooring, occurs only intermittently and at irregular intervals.

Tests on Flooring

The apparatus as originally set up for tests on flooring and shown in Figure 1 was as follows:

A 0.75-horsepower motor operating through a speed reducer was set up to produce reciprocating motion of an arm, operating at 30 cycles per minute. The arm carried the abrading element with an additional weight imposed so that the total weight of the abrading element was 3000 grams. The abrading element itself consisted of a block of appropriate material, the surface of which measured 15 cm. (6 inches) long and 2.5 cm. (1 inch) wide. This moved lengthwise over the face of the specimen being tested. The machine gave a stroke of 30 cm. (12 inches), so that abrasion occurred over a strip about 45 cm. (18 inches) long with the center of this strip receiving the greatest amount of wear. If desired this strip might be composed of two materials of not vastly dissimilar hardness in order to compare their rate of wear at the same time, such as of black and of white marble to be laid in alternating blocks.

The selection of the weight is a compromise. The weight to be used must not be so great as to cause active contact of the abrading element with the flooring. Rather it should be cushioned by the fine dust resulting from the wear, or by abrasive supplied. Observation shows that the movement of a shoe over the flooring, which is believed to be the time of greatest wear, is before the major portion of the weight is applied and as the foot is being lifted. For those reasons a weight slightly over 1 pound per square inch was used instead of the estimated 10 pounds per square inch present when the weight is all on one foot. Naturally, many variables, such as rubber and leather heels, women's small heels, etc., must be blended into the composite. Except in the case of actual slippage, the foot does not move after the full weight is applied and the heel touches the floor.

It should also be noted that the abrading member passes over the floor being tested at the rate of 60 times per minute, so that even with the lesser weight the rate of wear would be expected to be considerable. In view of these considerations conservatism dictates a tendency towards low rather

than high pressure as well as towards mild rather than harsh abrasive for the study of normal wear.

The specimen to be tested was marked off into 5-cm. (2-inch) sections along the 45-cm. (18-inch) strip. The depth of wear after given periods of operation of the abrading arm was measured in each section of the worn strip by a stud micrometer suitably mounted in a frame constructed for the purpose. The micrometer was sufficiently delicate so that measurements were reproducible to 0.0025 cm. (0.001 inch). Any material, such as flooring, on which measurements of abrasive

resistance are to be made, generally has different characteristics at the surface than in the body of the stone. Usually the surface is harder, and there are also minor surface irregularities. The same would be the case with nearly any flat solid. Therefore, a firmly bonded silicon carbide block was used as the abrading element. This caused the initial cut in the surface to be obtained quickly, as desired. The space between the abrasive crystals in the block soon become filled with powder derived from the specimen and thereafter the abrasive action is similar to that obtained in actual wear. Examination shows that the abrading member is not in contact with the flooring after this initial period, but is riding on a layer of dust particles derived from the flooring which are in turn the actual abrading agent, just as in stepping on the floor the abrading agent is the fine dirt, not the shoe.

The rate of wear at the very beginning of the test is not representative and would not be, even if the abrading element were already filled with debris from the specimen. The rate of wear in the remainder of the test is substantially constant and the abrasive action then occurring may be reasonably assumed to have a constant ratio to the rate of natural wear. After some time the silicon carbide block becomes impeded by excessive accumulated particles on the surface of the specimen, so that it is desirable to brush off this accumulation at regular intervals depending on the nature of the surface. The block itself should not be brushed and thus actual abrasion by the block is avoided. To accelerate the test further and thus measure drastic wearing conditions, the normal detritus from the floor could be replaced by a layer of abrasive such as emery, replaced at suitable intervals as in the Dow apparatus (1).

The apparatus may be operated for as long a period as seems desirable for the particular material under study. The study for which the machine was originally designed was a comparison between the wearing qualities of travertine marble and an artificial travertine made of a magnesium oxychloride cement composition. For this purpose the maximum period of operation was a total of 60 hours and the minimum 18 hours, depending on how quickly an appreciable wearing effect was obtained. In all cases the machine was stopped and the surface brushed off at 6-hour intervals, measurements of the depth of wear being made at those times.

Results were expressed in terms of depth of wear per hour as calculated from the micrometer measurements at 6-hour intervals. If preferable, of course, the loss in weight or in volume in a given period could be determined instead. Using the micrometer readings on the center sections of the specimen where the wear was deepest, and eliminating the first readings obtained before the rate of wear became constant, representative values for the two types of flooring material were as follows:

Travertine	0.1067 mm. (0.0042 inch) wear per hour
Artificial travertine compared	0.0254 mm. (0.0010 inch) wear per hour

Accumulation of extensive data showing the rate of wear at various points on the stone was found unnecessary after adequate data for interpretation had been assembled. Correlation between different determinations was very satisfactory, considering the type of determination. The results quoted have, of course, no general applicability but refer only to relative values on the types of material compared.

These results, obtained several years ago, have been confirmed qualitatively by observations on floors in use. No method of exact measure of rate of wear has been applicable to floors under our observation.

Kessler (5) points out the variable effect of humidity on the abrasive action in his apparatus and specifies that comparative tests should be run at the same relative humidity. No attempt was made to control the humidity in this study, and minor irregularities in the results may have been due to this cause. Since the authors' machine was operated for a period of 18 to 60 hours in comparison with Kessler's test period of 5 minutes, variation in humidity was not as important and the average rate of wear over the entire test period was consistent. As another comparison this equipment performed 30,000 to 100,000 complete cycles as compared with 225 to 6000 for the other types of equipment referred to.

The effect in wet wear would be expected to be less than when dry, because the water film would interfere with the contact between the finely divided particles and the stone. This was substantiated. For determinations of wet wear a separatory funnel was arranged to drip water continuously on the surface of the specimen, so that it was kept wet throughout the test period. The results under these conditions showed that after the rate of wear became constant it amounted to less than 0.00254 mm. (0.0001 inch) per hour for both travertine and the artificial travertine.

Glass Blackboard Tests

While this apparatus was originally developed for use on flooring materials, it was found to have more general applicability. As an example, the apparatus has been used to study the behavior on wearing of a composition glass blackboard. In that case, it was possible to exert abrasive action corresponding very closely to that occurring in use. In place of the silicon carbide block, an ordinary 6.25 × 15 cm. (2.5 × 6 inch) blackboard eraser was mounted at the end of the arm. The eraser was filled with chalk beforehand and chalk powder was spread on the surface of the piece of blackboard being tested. The eraser was loaded with a weight of 2 kg. and a pad of cloth placed under the sample

to take up any irregularities in pressure. The excess chalk on the surface of the sample was removed and a fresh supply added every 6 hours throughout the test. No quantitative measurement of the results was made in these tests, as the primary interest was in the appearance and writing surface of the boards after an extended period of use. Instead, the macroscopic and microscopic appearance of the blackboard surface, with and without chalk, were recorded photographically as previously published (8). Micrometer measurements might be made in the same way as on the flooring if desired. On the basis of an estimate of the average amount of erasing a blackboard receives in schoolroom use, it was calculated that an hour's operation of the machine corresponded to approximately 2 years of actual service.

Abrasive Efficiency of Tooth Pastes

Still another application of the apparatus, and one certainly far removed from tests on flooring, was its use to compare the relative abrasive efficiency of tooth pastes. In this instance, the interest was in comparison of different abrasives against a standard surface, rather than comparison of the resistance of different surfaces to a standard abrasive. A much smaller machine was built for this purpose, following the same principles as those already described for the larger machine. The miniature apparatus is illustrated in Figure 2.

A 0.25-horsepower motor, *a*, is attached to the gear-reducing unit, *b*. Through the eccentric, *c*, and connecting rod, *d*, the abrading element is given a reciprocating motion of about 100 strokes per minute. The steel plunger, *d'*, fits snugly into the metal shoe, *e*, the bottom of which is surfaced with a plate glass. The plunger is guided by a brass tube, *f*. A glass plate, *g*, carrying the surface to be abraded, *h*, is held in place by two iron clamps, *i*. The combined weight of the plunger and metal shoe gives a load of 160 grams.

Abrasives are present in tooth pastes in order to remove the film of mucin which builds up on the teeth. They must be sufficiently abrasive to be effective but not so drastic as to injure the teeth. The standard surface against which the tooth pastes were compared consisted of a mucin plaque prepared as follows. A suitable quantity of mixed human saliva was collected and centrifuged to throw down the mucin (4). This mucin was then spread upon a thoroughly clean flat glass plate as evenly as possible. When nearly dry, it was subjected to the vapors of formaldehyde for several hours in order to form a hard, tough film, corresponding closely to the mucin films formed on the teeth. The plaques so produced were about 10 cm. (4 inches) square, and each was marked into four equal sections.

In order to simulate conditions of use exactly, the abrading element would have to be a brush, corresponding to a tooth-brush. However, use of a brush would introduce the complication of having varying amounts of the different tooth pastes run up into the bristles and out of contact with the mucin plaque. A glass surface was therefore used as one offering no variables.

In carrying out the tests, definite quantities of tooth paste were intimately mixed with fresh human saliva and the mixture was deposited on one section of the mucin plaque. Similar mixtures of other tooth pastes to be compared were deposited on the other sections of the plaque. The plaque was then set in place in the machine and abrasion applied to the extent of 100 strokes of the arm on each of the four sections. At the end of the operation the plaque was removed, rinsed gently, and the four sections compared as to relative degree of removal of the film and presence or absence of striations. The results obtained showed definite and reproducible differences between the tooth pastes compared.

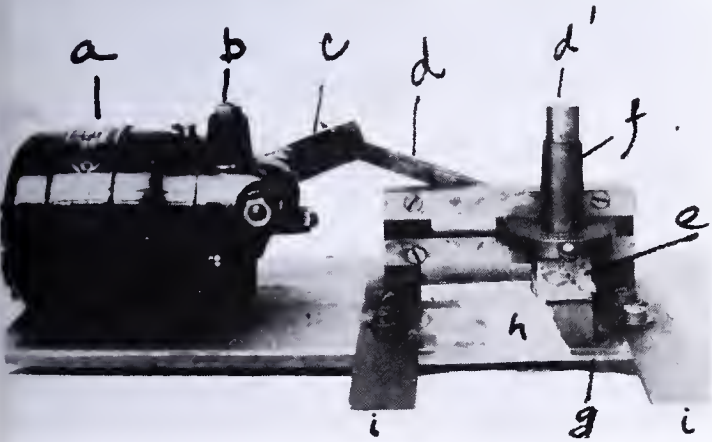


FIGURE 2. MINIATURE APPARATUS

In terms of any one accepted as standard, greater or lesser abrasion can be obtained and recorded photographically.

Summary

The apparatus described presents a method of relative comparison of wear on materials. It is known to be in use in industry but not previously described and has the following advantages:

Normally a mild rate of wear is obtained, but this can be varied if desired.

No special equipment is required for preparation of the specimen.

Adjacent blocks to be laid alternately in the same floor can be compared.

The equipment is easily assembled in any laboratory.

The large number of cycles tends to eliminate accidental variations.

With suitable modification it is applicable to many types of materials.

It has the following disadvantages:

The large number of cycles requires a substantial time for the operation.

A large specimen is required for the full-size machine.

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An Inorganic Liquid Mixture for Temperature Baths in the Range 100° to 250° C.

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IT IS common laboratory practice to employ for temperature baths in the range 100° to 300° C. sulfuric acid, paraffin oils, bath waxes (5, 8), or fusible alloys (3, 6, 7, 9), all of which are subject to rather serious limitations. In regard to other materials (1, 2, 4) which can be used, the literature is indeed meager.

In connection with some work on organic oxidations it was necessary to employ a bath having the following specifications: (1) temperature range 125° to 250° C., (2) relatively high heat capacity, (3) no fuming at the temperature of operation, (4) transparent after long usage, (5) material easy to remove from glassware, and (6) offering no fire hazard.

The organic substances which are usually employed in the work do not meet the five latter requirements. Of the inorganic materials, only the fusible alloys and sulfuric acid can be used in this range. Metal baths are objectionable on two counts: their relatively low heat capacities and high specific gravities. Sulfuric acid is rather satisfactory except that, on account of fuming, its use is limited to the hood, and some danger is entailed in handling it while hot.

Since the usual fusible salts cannot be employed in this range, other inorganic substances were investigated. Of these, ortho- and metaphosphoric acids appeared to have many desirable properties. Metaphosphoric acid forms a clear liquid above 150° C. which solidifies on cooling. A series of experiments was conducted using 85 per cent orthophosphoric acid as a diluent.

Experimental

Mixtures containing various amounts of 85 per cent orthophosphoric acid to a given weight of metaphosphoric acid were prepared. Before being employed in the bath, each was given an initial heat treatment, which consisted of raising the temperature slowly to 260° C. and holding until rapid evolution of steam had ceased. After this treatment, the solutions appeared to possess constant thermal properties.

Test runs were made on various mixtures which had received this treatment, to determine which were most suitable for use over the given temperature range. The results are tabulated in Table I.

TABLE I. TEST RUNS

No.	Composition by Weight 85% H ₃ PO ₄	Weight HPO ₃	Maximum Temperature Before H ₂ O evolved on second heating ° C.	Before fuming ° C.	State at Room Temperature
1	1	1	Above 250	340	Solid
2	2	1	Above 250	340	Viscous
3	3	1	Above 250	340	Less viscous
4	4	1	Above 250	340	Mobile
5	6	1	Above 250	340	Mobile

For most purposes No. 4 seemed highly satisfactory, in that it is liquid at room temperature. No. 2 can be used more satisfactorily in the higher temperature ranges up to 340° C. but is solid at 20° C. A bath such as No. 3 has been used for over a month in this laboratory with no apparent change in properties.

These liquids, in addition to satisfying all the aforementioned requirements, possess a very small temperature gradient, as rising temperature causes expansion which results in the circulation of the liquid.

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Volumetric Determination of Sulfate in Water

The Barium Chromate Method

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THE barium chromate method for the volumetric determination of sulfate was proposed in 1889 by Andrews (1), who stated "The process depends upon the following series of reactions: First, to the solution of a sulfate is added an excess of a solution of barium chromate in hydrochloric acid; second, the solution is neutralized with ammonia or calcium carbonate and filtered; third, the filtrate is acidified with hydrochloric acid, potassium iodide added, and the free iodine titrated with decinormal sodium thiosulfate solution."

This description implies exact equivalence between the chromate determined by titration and the sulfate originally present in the sample. Under the conditions of the determination, however, barium chromate is slightly soluble. Several investigators (2, 3) have recommended the use of a blank obtained by carrying a definite portion of the reagent solution through the procedure used by them, to correct for the barium chromate dissolved under the conditions of the determination and, therefore, once determined, applicable in all subsequent determinations of sulfate by the method. This is true if the reagent is free of impurities. Most of the barium chromate available on the market, however, contains either soluble barium salts or soluble chromates, usually the latter. In order to eliminate error from these sources it is necessary to determine the thiosulfate requirement of each new reagent solution made up, or first to free the barium chromate of impurities and then apply a correction for the barium chromate dissolved under the conditions of the determination. As the use of a blank is necessary in either case, it has been found more practical in this laboratory to purify the barium chromate partially before the preparation of the reagent solution by a simple process, in order to reduce the quantity of soluble chromate or soluble barium salts present, and then to determine the blank on each new reagent solution made up. The blank represents in this case barium chromate soluble under the conditions of the determination plus soluble chromate in the reagent or minus an amount of soluble chromate equivalent to soluble barium salts in the reagent.

Purification and Preparation of Reagent

Dissolve 25 grams of barium chromate in *N* hydrochloric acid, make the volume up to approximately 2 liters with distilled water, precipitate the barium chromate with ammonium hydroxide, wash three or four times by decantation with distilled water, and redissolve in as little *N* hydrochloric acid as possible. Determine the strength of the solution iodometrically (using 5 ml.) and dilute so that 1 liter contains approximately 7.5 grams of barium chromate. A dilution of four times is usually necessary to obtain a solution of this strength, making the acidity 0.25 *N*.

Determination of the Blank

Carry a series of samples containing known amounts of sulfate (5, 10, 15, and 20 mg.) through the procedure for the determination of sulfate. The difference between the thio-sulfate titration for the 5-mg. SO_4 sample and that for the 10-mg. sample represents the amount of thiosulfate required by chromate equivalent to 5 mg. of SO_4 . This volume, subtracted from the titration obtained on the 5-mg. sample, gives the volume of thiosulfate solution required for dissolved barium chromate and soluble chromate in the reagent. Similar calculations for the titrations on the other samples give a series of results from which to calculate the average blank.

The following slightly modified procedure, with the use of

a blank determined as described, has been found to give results consistent with those obtained gravimetrically.

Procedure

Measure 100 ml. of the water sample into a 250-ml. Erlenmeyer flask and make just acid to methyl orange (1 drop) with *N* hydrochloric acid, added dropwise. Add, at room temperature, 10 ml. of barium chromate solution (7.5 grams of barium chromate in 1 liter of 0.25 *N* hydrochloric acid). Allow the sample to stand 10 minutes, swirling the flask several times during this period. Precipitate the excess barium chromate with ammonium hydroxide, adding 3 drops in excess of the amount necessary to change the color from orange yellow to lemon yellow (a total of 6 drops is usually sufficient when 10 ml. of the chromate reagent are used for the precipitation), and again allow the sample to stand 10 minutes, swirling and shaking several times as before. The swirling accelerates coagulation, so that the subsequent filtration is rapid and clean. Filter, catching the filtrate in another 250-ml. Erlenmeyer flask, and wash the precipitate several times with a fine stream of distilled water. Add to the filtrate 10 ml. of 10 per cent potassium iodide solution and 2 ml. of hydrochloric acid (sp. gr. 1.18 to 1.19) and mix carefully with a glass stirrer. After 10 minutes titrate, while rotating the flask gently, with 0.05 *N* sodium thiosulfate (1 ml. = 1.64 mg. of SO_4), using starch solution as indicator. From the milliliters of thiosulfate required for the titration subtract the blank, previously determined, and multiply the remainder by 16.4 (if a 100-ml. sample has been used) to get parts per million of SO_4 .

One hundred water samples on which the sulfate had been determined gravimetrically in the course of regular complete analysis were tested by the procedure and the use of a blank determined as described in this paper. The samples tested contained from 2 to 1786 parts per million of SO_4 , but for each test a volume of the sample containing not more than 25 mg. of SO_4 was used. The results obtained, compared with the gravimetric results on the same sample, are shown in Figure 1. The value (in mg. of SO_4) used for plotting was the SO_4 content of the sample taken for the test. With few exceptions the results obtained by the barium chromate method check those obtained gravimetrically within ± 0.2 mg.

The interfering effects of aluminum, zinc, nickel, and iron have been mentioned by various investigators. Natural waters, however, rarely contain more than a few tenths of a part per million of aluminum, zinc, or nickel, and an examination of more than 650 analyses of waters from all parts of the United States shows that in practically all alkaline waters iron in excess of 0.1 part per million is precipitated within a few hours after the waters come from the ground. These constituents might, however, be present in other substances tested in quantities sufficient to affect the results. Calcium,

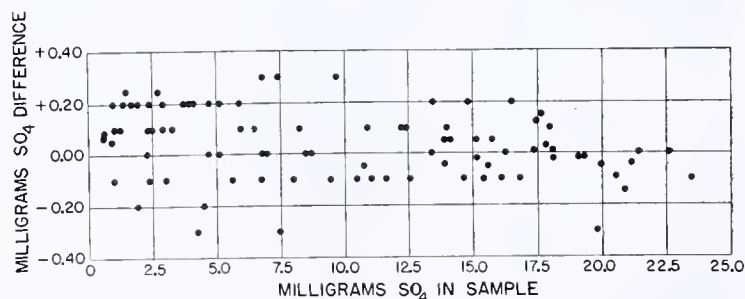


FIGURE 1. DIFFERENCE BETWEEN RESULTS FOR SO_4

Difference in results obtained by chromate method and those obtained gravimetrically in the course of regular complete analyses of water samples.

Colorimetric Estimation of Peroxides in Unsaturated Compounds

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THE chief methods of estimating the peroxides in unsaturated organic compounds are based on the oxidation of either potassium iodide or a ferrous salt by the peroxides. For example, Marks and Morrell (2) use a solution of potassium iodide in glacial acetic acid. After the iodine is liberated, the solution is diluted with water and the free iodine titrated with standard sodium thiosulfate. A considerable error may be introduced by the addition of iodine to the unsaturated linkage, particularly since the rate of addition in many cases is greatly accelerated by the presence of peroxides.

Yule and Wilson (3) estimate peroxides in cracked gasoline by shaking it with an acidified solution of ferrous sulfate and ammonium thiocyanate in a 50 per cent acetone-water mixture. The ferric thiocyanate which is formed is titrated with a standard titanous chloride solution. Several improvements in this method are desirable. Instead of using as the solvent 50 per cent acetone, in which most hydrocarbons have a limited solubility, it is preferable to use a solvent which is miscible with hydrocarbons. It is also desirable to estimate the ferric thiocyanate formed by the peroxides by some means other than standard titanous chloride, in order to avoid the difficulties inherent in the use of this reagent. Since minute quantities of ferric thiocyanate produce an intense coloration when in solution, it is possible and advantageous to determine the ferric thiocyanate colorimetrically. The convenience and rapidity of colorimetric procedures are well known.

In selecting a solvent there are two important factors to be considered: (1) the solvent should dissolve an appreciable quantity of the inorganic salts used, and (2) the solvent should be miscible with the organic compounds which are to be analyzed. Absolute methyl alcohol meets these requirements.

Preparation of the Reagent

The reagent is prepared by dissolving 5 grams of ammonium thiocyanate and 5 cc. of 6 *N* sulfuric acid in 1000 cc. of absolute methyl alcohol, and then saturating the solution with pure ferrous ammonium sulfate. Shaking the solution with the finely pulverized salt for a few minutes is sufficient. The faint pink color which is formed may be evaluated by comparing it with a suitable color standard. The results of analyses may then be corrected for the trace of ferric thiocyanate present in the reagent. The faint pink color in the reagent does not deepen appreciably over a period of an hour or so. The usefulness of the reagent may be extended to much longer periods by keeping the reagent in an inert atmosphere.

Preparation of the Color Standard

Solutions of ferric thiocyanate in absolute methyl alcohol are used as color standards. In order to make the colorimetric comparisons conveniently and accurately, the concentration of the standard solution should not differ more than two- or threefold from that of the solution whose color is being determined. Furthermore, since solutions of ferric thiocyanate in methyl alcohol fade slowly on standing, the standard solutions should be freshly prepared each day. This may be accomplished by adding ammonium thiocyanate and sulfuric acid, in the same proportions used in preparing the reagent, to standard solutions of ferric chloride in absolute

methyl alcohol. For colorimeters of the Duboscq type, it is recommended that the concentrations of the ferric chloride solutions range from 0.00004 to 0.001 mole per liter. Three concentrations are sufficient for ordinary purposes. In case any ferric chloride has been reduced to the ferrous state, a small amount of active peroxide may be added.

Procedure

If the compound being analyzed is a liquid having a moderate peroxide concentration, it is added directly to the reagent by means of a small pipet or buret. Otherwise a solution in absolute methyl alcohol is made, and the concentration so adjusted that, when quantities of the solution ranging from 0.05 to 0.5 cc. are added to 10-cc. portions of the reagent, a color equivalent to 0.00002 to 0.0002 mole of ferric thiocyanate per liter is produced. With many compounds, such as butylacetylene and 1-hexene, the color reaches a maximum intensity within a few seconds, and the solution is then immediately compared with a color standard having approximately the same concentration. Some peroxides, such as the one found in diamylene, react with the reagent rather slowly. In such cases the reaction may be greatly accelerated by heating the solution to just below boiling for 4 or 5 minutes. The quantity of peroxide detected by this method is proportional to the amount present in the solution. The results of an analysis are reproducible.

Discussion

Potassium iodide is more easily oxidized than is ferrous sulfate, as the molal electrode potentials of the ferrous and the iodide ions show. Certain peroxides, such as benzoyl peroxide, readily liberate iodine from potassium iodide, but react extremely slowly, if at all, with ferrous sulfate. Consequently, if some organic material contains a wide variety of peroxides, it is possible that a portion of the peroxides is not determined by a method using a ferrous salt as the reducing agent. Yule and Wilson (3) found that after an exhaustive treatment of cracked gasoline with ferrous sulfate, there still remained a small amount of peroxide which oxidized potassium iodide. Nevertheless, since potassium iodide cannot be used with many peroxides of unsaturated compounds, the ferrous sulfate methods are very useful for comparative purposes even where complete reduction of all peroxides is not obtained.

TABLE I. COMPARISON OF METHODS

	Yule and Wilson	Colorimetric
Cracked gasoline	0.025	0.036
Butylacetylene	0.23	0.29
Diamylene	0.30	0.54

The accuracy of the colorimetric method presented here has been studied by means of dilute solutions of hydrogen peroxide of known concentrations and by means of pure preparations of succinyl peroxide ($\text{HOOC} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COO}$)₂. For example, the concentration of a hydrogen peroxide solution as given by the standard potassium permanganate method was 0.0279 mole per liter, while the colorimetric procedure gave 0.028 mole per liter. The succinyl peroxide was prepared by the method of Clover and Houghton (1), and was recrystallized twice from acetone. The calculated weight per cent of active oxygen in succinyl peroxide is 6.83 per cent; obtained 7.0 per cent.

For fuller evaluation of the merits of the colorimetric procedure, it was compared with the method of Yule and Wilson (3). In calculating the results of an analysis, the reasonable

assumption was made that each mole of peroxide reacted with two equivalents of ferrous sulfate. The comparison of the two methods is presented in Table I, the results being reported in terms of gram equivalents of active oxygen per liter of hydrocarbon.

The lower results given by the method of Yule and Wilson are probably due to the incomplete reduction of the peroxides, for the reacting substances are, on the whole, concentrated in two different layers. The more peroxide there is present, the more difficult it becomes to obtain a quantitative reduction. Yule and Wilson have noted that an increase in peroxide concentration does not give a proportionate increase in the quantity of peroxide detected by their method.

Summary

A method is presented for the colorimetric estimation of peroxides in unsaturated organic compounds, based on the oxidation of ferrous sulfate in the presence of ammonium thiocyanate, using absolute methyl alcohol as the solvent.

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RECEIVED January 22, 1936.

Volumetric Determination of Iodides by Ceric Sulfate

An Application of the Indicator *o*-Phenanthroline Ferrous Ion

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THE direct oxidative titration of iodides to a visual end point depends, in most procedures, upon the conversion of the initially liberated iodine to the cationic or covalent state. The end point is the disappearance of iodine, and it is in the manner of determining this disappearance that the various methods differ. Each is subject to certain disadvantages, either of manipulation or of estimating the end point.

In Andrews' method (1) an immiscible organic solvent, such as chloroform, must be used to detect the oxidation of the iodine to iodine monochloride. Addition of oxidizing agent, with shaking after each addition, is continued until the violet iodine color is discharged from the layer of inert solvent. Lang's procedure (6) is more direct. Titration is continued to the disappearance of the blue starch-iodide color which occurs at the conversion of the iodine to iodine cyanide. To minimize the danger of working with an acid solution of a cyanide, it is necessary to use long, narrow-necked flasks. In Berg's method (2) the iodine liberated in the oxidation reacts with acetone to form iodoacetone. Starch is the indicator. As the end point is approached each drop of oxidizing agent produces a blue color which is slowly discharged. The end point is reached when further addition of oxidant no longer produces a blue color. The most common oxidizing agent is potassium iodate, although Swift (7) has shown that potassium permanganate, potassium dichromate, and ceric sulfate can be used in the Andrews procedure, and Berg (3) has shown the utility of potassium bromate in the cyanide method.

In the method to be described the disadvantages of these methods are eliminated by avoiding the use of an iodine end point. A previous attempt in this direction was made by Hahn and his co-workers (5), who proposed titration to a permanganate end point, without, however, eliminating the inconvenience of a two-phase system. The iodine liberated in the oxidation had to be extracted (with ethyl acetate) to permit detection of the end point.

The present method is based upon Berg's procedure for the elimination of iodine by the acid catalyzed iodination of acetone. By the use of ceric ion as oxidizing agent and *o*-phenanthroline ferrous ion as indicator, the titration of iodides can be performed rapidly, precisely, and accurately.

Reagents

Two ceric sulfate solutions were prepared by dissolving ceric ammonium sulfate in *M* sulfuric acid, and were standardized

against sodium oxalate by the method of Walden, Hammett, and Chapman (8). Solution I was 0.1074 *M*; solution II, 0.09982 *M*.

An approximately 0.1 *M* solution of purified potassium iodide was used throughout these experiments. It was standardized against the ceric sulfate solutions, the end point being determined electrometrically—a procedure shown to be exact by Willard and Young (9).

Acetone was of reagent grade and the potassium bromide, sodium chloride, and sulfuric acid were of c. p. grade. Blanks on these materials in the amounts used in the experiments required a fraction of a drop of ceric sulfate to change the color of the indicator.

The solution of *o*-phenanthroline ferrous sulfate was 0.025 *M*.

Method of Analysis

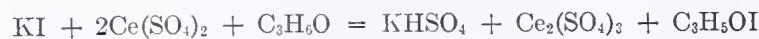
A measured volume of the iodide solution is treated with 25 ml. of acetone, 10 ml. of 9 *M* sulfuric acid, and water to make the volume 100 ml. After adding one drop of *o*-phenanthroline ferrous sulfate solution, the mixture is titrated with the ceric sulfate until the pink color of the indicator changes to a pale blue. The end point is sharp and lasts several minutes.

The rate at which the oxidant is added does not affect the results. At the start of a titration rapid addition of the ceric sulfate may cause the solution to be colored brown by free iodine, which rapidly disappears on interrupting the titration and stirring a few seconds. It is desirable to conduct the titration in flasks, since iodoacetone is a lachrymator.

Results

Table I illustrates the precision with which this titration can be performed. There is no difficulty in obtaining checks better than one part per thousand.

From these results the normality of the iodide solution is found to be exactly twice the molarity as determined potentiometrically. Assuming moniodination of the acetone, the reaction may be represented as



It is unnecessary to adhere strictly to the conditions for the titration as given above. Equally good results are obtained if 5 or 15 ml. of acid are used or if the solution is diluted. Such changes merely affect the rate of reaction of the iodine

TABLE I. PRECISION ATTAINABLE

Potassium Iodide Ml.	Ceric Sulfate Ml.
	Solution I, 0.1074 M
10.00	18.67
	18.69
	18.70
	18.69
	18.70
	Av. 18.69
	Av. deviation 0.8 part per 1000
	Solution II, 0.09982 M
10.00	20.10
20.00	20.10
5.00	40.20
	10.04
	Av. deviation 0.1 part per 1000

TABLE II. EFFECT OF VARYING CONCENTRATION OF ACID AND VOLUME OF SOLUTION

(10.00 ml. of potassium iodide and 25 ml. of acetone in each titration. Ceric sulfate required, 18.69 ml.)

Volume at Start Ml.	9 M H ₂ SO ₄ Ml.	Ceric Sulfate Used Ml.
100	1	18.75
100	5	18.70
100	15	18.68
100	20	18.61
145	30	18.60
100	30	18.43
200	20	18.69

TABLE III. EFFECT OF BROMIDE

(10.00 ml. of potassium iodide and 25 ml. of acetone in each titration. Ceric sulfate required, 18.69 ml.)

0.1 M KBr Ml.	Volume at Start Ml.	9 M H ₂ SO ₄ Ml.	Ceric Sulfate Used Ml.
5	100	10	18.70
10	100	10	18.72
15	100	10	18.85
10	200	20	18.68
15	200	20	18.71
20	200	20	18.75
30	300 ^a	30	18.72
50	309 ^a	30	18.76

^a 35 ml. of acetone.

with the acetone, which is proportional to the concentration of acid and of acetone (4). Too little acid is undesirable, since it leads to slightly high results and the titration is time-consuming, while too high a concentration of acid leads to

low results and a fleeting end point. The data in Table II show the effect of varying these conditions.

EFFECT OF BROMIDE. Measured volumes of 0.1 M potassium bromide were added to the iodide and the titration was performed as described above. In general, more ceric sulfate is required than for iodide alone. The larger the ratio of bromide to iodide, the greater is the excess of ceric sulfate necessary to reach an end point lasting 1 minute. This interference can be almost entirely eliminated by diluting the solution sufficiently while keeping the acid concentration approximately constant. Within the limits investigated it was possible to titrate the iodide with an accuracy of 3 to 4 parts per thousand when the bromide-iodide ratio was 5 to 1. The results of several of these titrations are given in Table III.

EFFECT OF CHLORIDE. Moderate amounts of neutral chloride do not interfere. Titrations in the presence of 0.5, 1.0, and 5.0 grams of sodium chloride required 20.10, 20.16, and 20.23 ml. of ceric sulfate, compared to 20.10 ml. for iodide alone. In the titration with 5.0 grams of chloride present, precipitation of the salt occurred. The excess ceric sulfate required with the larger amounts of chloride may be due to the formation of hydrochloric acid, since titrations of iodide alone in which hydrochloric acid was substituted for the sulfuric acid used excess ceric sulfate.

Summary

In the presence of acetone and sulfuric acid iodides may be titrated quantitatively with ceric sulfate to a visual end point, using *o*-phenanthroline ferrous ion as indicator. The effect of bromides and chlorides on this titration has been determined.

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Standardization of Sodium Thiosulfate Iodometrically against Copper

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THE method of standardizing sodium thiosulfate against copper and of determining copper in samples which are soluble in nitric acid as outlined by Gooch and Heath (1) requires long evaporations. Kendall (2) has pointed out that these evaporations eliminate nitrous acid. The use of urea for the elimination of nitrous acid was worked out independently by the author. Afterwards, in a careful study of the literature it was found that Koelsch (3) suggested a procedure essentially the same as that given below and that Pozzi-Escot (4) also suggested the use of urea, employing, however, a much longer procedure. It is felt that this simple method has been overlooked and should be called to the attention of the analytical chemist. Results with this method agree with those of Gooch and Heath (1) within one part per thousand.

Procedure

Weigh a sample of pure copper, 0.2 to 0.3 gram. Dissolve the sample in 2 to 5 ml. of concentrated nitric acid. Add 0.5 gram of urea and heat to boiling. Cool, adjust the acidity by adding 6 N ammonium hydroxide until a white precipitate is formed, dissolve the precipitate with 6 N acetic acid, and add 5 ml. in excess. Add 3 grams of potassium iodide, allow to stand 2 minutes, and titrate the liberated iodine with sodium thiosulfate solution. Starch is used as an indicator (2 ml. of 1 per cent solution) and should be added about 1 ml. before the end point is reached.

Variations in concentration of NO₃⁻ and NH₄⁺ have no effect on the final precision.

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Microdetermination of Ammonia Nitrogen in Eggs

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INTERIOR quality of shell eggs is commonly and most conveniently determined in commerce upon the unopened egg by means of candling. Physical methods that measure quality more precisely have been described for eggs which may be broken out (3, 4). Chemical methods have not found application in this field except for comparatively few studies of the loosely bound nitrogen (2, 5). The chemical procedure hitherto followed has been an adaptation of the Folin aëration method for ammonia in urine—that is, aëration of an alkaline solution of the material, absorption of the ammonia by excess standard acid, and its subsequent determination by titration or nesslerization.

The aëration method has many disadvantages, especially when applied to the estimation of the extremely small amounts of ammonia in egg materials. It involves a complicated setup of wash bottles, aëration tubes, absorption tubes, manometers, pressure regulators, and traps, since the volume of air, its rate of flow, and its pressure must be carefully regulated and its freedom from ammonia insured (2, 5). Excessive foaming must be prevented, which is very difficult with egg materials. The time involved for aëration is between 4 and 5 hours, and the attention of the operator is required during this period.

To overcome the inconvenience of the aëration method an attempt was made to use the absorption process described by Conway and Byrne (1), but it was found necessary to modify this procedure to adapt it to the purpose at hand. The principle involved is the liberation of ammonia by a saturated potassium carbonate solution and its absorption in standard acid as before, but instead of its removal by aëration, the volatility of the ammonia is employed for this purpose.

Apparatus

Cells were made from tops of 10-cm. Petri dishes. The rims of these dishes were ground to a smooth surface on a piece of plate glass with the aid of fine Carborundum powder and water. Glass rings 5 cm. in diameter and of a height slightly less than that of the side walls were centered in the dishes and sealed in place with de Khotinsky cement, which in turn was coated with beeswax to protect the cement from the alkali used. This wax coating had to be renewed at intervals. An all-glass cell proved very satisfactory but was unduly expensive. Covers were glass plates with a ground

A method for the determination of ammonia nitrogen in eggs without aëration is described. The ammonia is absorbed in standard acid from a thin layer of an alkaline solution of the sample in a modification of the Conway-Byrne cell. It has many advantages over the troublesome aëration methods in that larger numbers of samples may be run simultaneously and the operation, control, and equipment are simpler. Data are presented to show the reliability and accuracy of the procedure. Directions are given for the fabrication of the modified Conway-Byrne cell.

chamber. Ostwald-Folin pipets were used to sample the egg material. Tips were adjusted to allow rapid delivery and they were then calibrated to deliver 5 cc. of egg white, yolk, diluted yolk, or mixed whole egg. An electrically heated cabinet kept at $38^{\circ} \pm 1^{\circ}$ C. by means of a thermostat was used to heat the cells for the required time.

Solutions Required

The acid used was 0.005 *N* hydrochloric acid, made by diluting 0.10 *N* hydrochloric acid, and contained the indicator. The indicator, adapted from that described by Tashiro and modified by Conway (1), was prepared by dissolving 0.08 gram of the sodium salt of methyl red and 0.02 gram of methylene blue separately in alcohol, mixing, and making up to 100 cc. with alcohol. One cubic centimeter of this solution was added to each 100 cc. of the standard acid before making to volume. With this indicator the end point was that point

at which the least color was present, the solution having a grayish tinge between the red of the acid and the green of the alkaline colors. The end point was very sharp and readily reproducible, titrations checking within 0.01 cc. The excess acid was determined by titration with 0.0025 *N* sodium hydroxide, also prepared by diluting a 0.1 *N* solution and standardized each day against the acid. A saturated potassium carbonate solution was used to liberate the ammonia from the egg mixtures. Ammonia-free water prepared by distilling distilled water containing a small amount of potassium acid sulfate was used throughout, and it

was found advisable to carry out the determinations in an ammonia-free atmosphere. Suitable blanks were run.

Method

This method was used for whites and yolks separately and for mixed whole eggs. The eggs to be examined were

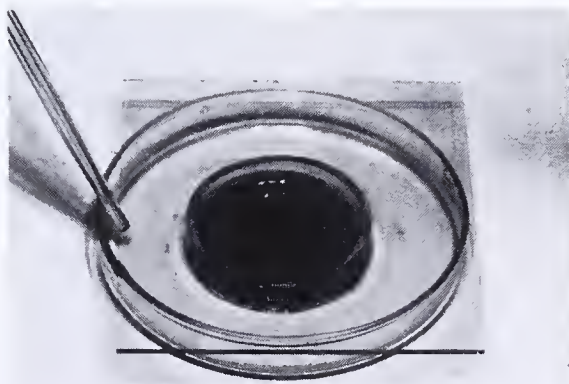


FIGURE 1. ABSORPTION CELL, INDICATING METHOD OF INTRODUCING MATERIALS

broken out into Petri dishes and samples taken as described below.

EGG WHITE. Place in the inner chamber 5 cc. of 0.005 *N* hydrochloric acid from a calibrated pipet and in the outer chamber approximately 2 cc. of ammonia-free water. Cover the cell. Slip the cover horizontally slightly to provide a narrow opening and add to the outer chamber 5 cc. of the liquid white from the pipet calibrated for this purpose. Close the cell and mix the contents by gently tilting and rotating. Introduce approximately 2 cc. of saturated potassium carbonate solution into the outer chamber and again mix the contents as before. Place the cells in stacks with a kilogram weight on top in the cabinet kept at 38° C. for 1.5 hours. At the end of this period, titrate the excess acid with 0.0025 *N* sodium hydroxide solution, and calculate the ammonia to milligrams of ammonia nitrogen per 100 cc. of egg white.

EGG YOLK. This procedure has been slightly modified by a preliminary dilution of yolk, since undiluted yolk does not mix properly with the carbonate solution under the conditions specified for egg white.

After removing the sample of white, slit the yolk membrane slightly with a small scalpel at the top of the yolk without removing the firm white. Thrust the Ostwald-Folin pipet with an enlarged tip through the opening, remove 5 cc. of yolk, and add to 3 cc. of ammonia-free water in a test tube. The yolk can be conveniently blown out by means of a rubber bulb attached to the pipet. After thoroughly mixing, introduce a 5-cc. aliquot with the pipet calibrated for diluted yolk into the outer chamber of a cell containing 5 cc. of the standard acid in the inner chamber. Add 3 cc. of the saturated potassium carbonate solution to the diluted yolk, close the cell, mix with the same rotary and tilting motion, and place in the cabinet with a weight for 1.5 hours at 38° C. As before, titrate the excess acid with 0.0025 *N* sodium hydroxide and calculate the ammonia to milligrams of ammonia nitrogen per 100 cc. of yolk.

MIXED WHOLE EGG. Mixed whole egg was prepared by breaking an egg in a 6-ounce wide-mouth glass-stoppered bottle and shaking it with four large glass beads. The procedure then used was practically the same as for egg yolk.

Deliver 5 cc. of mixed whole egg with the Ostwald-Folin pipet calibrated for mixed whole egg into the outer chamber of a cell which contains 5 cc. of the standard acid in the inner chamber. Add 3 cc. of the saturated potassium carbonate solution, close the cell, mix by tilting and rotating, and place in the cabinet for 1.5 hours at 38° C. Titrate the excess acid and calculate in terms of milligrams of ammonia nitrogen per 100 cc. whole egg.

Experimental

Conway and Byrne (1) have suggested alternative sets of conditions for the quantitative absorption of ammonia, stipulating 1.5 hours at room temperature or 1 hour at 38° C. The ammonia nitrogen is so low in fresh eggs that larger samples are required than can satisfactorily be handled in the Conway-Byrne unit. With the modification of the unit suggested in this paper the interrelationships of time, temperature, and linear dimensions of the inner and outer chambers require a longer period or a higher temperature than that specified by Conway and Byrne. In practice, holding periods at room temperature up to 3 hours or at 38° C. less than 1.5 hours did not provide suitable conditions for recovery of ammonia from egg materials. As a result a period of 1.5 hours at 38° C. was chosen.

The volume of saturated solution of potassium carbonate required was determined by experiment with white and yolk, keeping other factors constant.

From Table I it was evident that the quantity of saturated solution of potassium carbonate could be varied considerably without changing the amount of ammonia liberated. Since it was desirable to keep the volume in the outer chamber as small as possible and there was no advantage in using larger volumes, it was deemed sufficient to use for the white 2 cc. of the saturated solution of potassium carbonate and for the yolk, 3 cc.

TABLE I. SATURATED SOLUTION OF POTASSIUM CARBONATE REQUIRED FOR COMPLETE EXPULSION OF AMMONIA

K ₂ CO ₃ Solution Used Cc.	Ammonia Nitrogen	
	White Mg./100 cc.	Yolk Mg./100 cc.
1		2.30
2	0.49	2.63
3	0.52	2.60
4	0.45	2.58
5	0.46	2.63

The possibility that ammonia might be liberated from yolk alone during the period of heating was investigated and the results are given in Table II.

TABLE II. EFFECT OF HOLDING YOLK AT 38° C. FOR 1.5 HOURS WITHOUT ADDITION OF CARBONATE SOLUTION

	0.005 <i>N</i> Alkali Required to Titrate Acid Cc.
NH ₃ -free water	4.52
	4.54
NH ₃ -free water + yolk	4.58
	4.54
	4.54
	4.52

Since titration values of the standard acid were the same with and without the yolk, it is certain that no ammonia was liberated by the yolk itself when held for the required time without the carbonate addition. This is probably due to the fact that yolk is naturally slightly acid, having a pH of approximately 6.0 when fresh which increases to about pH 6.8 after long periods of storage.

The absorption period was established as the time required for the recovery of ammonia from a standard ammonium sulfate solution at 38° C.

TABLE III. TIME NECESSARY FOR COMPLETE REMOVAL OF AMMONIUM NITROGEN FROM AMMONIUM SULFATE SOLUTION

(Results expressed as milligrams of ammonia nitrogen in 100 cc. of solution.)

Time at 38° C. Hours	Concentration of Solution Used	Concentration of Solution by Actual Determination
0.5	4.11	2.45
1.0	4.11	3.56
1.5	4.11	4.07
2.0	4.11	4.03

Since an absorption period of 1.5 hours gave practically the theoretical value for the ammonia nitrogen recovered, this time was used for all the experiments.

The recovery of ammonia from a standard ammonium sulfate solution replacing yolk or when added to yolk was found to be satisfactory. Varying quantities of a standard ammonium sulfate solution were used in a series of determinations to produce concentrations similar to what might be expected in egg yolk.

TABLE IV. RECOVERY OF AMMONIA NITROGEN FROM A STANDARD SOLUTION OF AMMONIUM SULFATE

No. of Detns.	Ammonia Added Mg./100 cc.	Nitrogen Recovered Mg./100 cc.	Standard Deviation
7	2.05	2.04	0.143
10	4.11	4.06	0.145
7	5.00	5.24	0.080
7	6.16	5.97	0.365

A comparison of the amounts added and recovered in Table IV shows satisfactory agreement.

When definite amounts of ammonia nitrogen were added to yolk and determinations made before and after the additions, the results shown in Table V were obtained.

In Table V three different quantities of ammonia nitrogen were added to aliquots of two lots of pooled yolk. The recovery of the ammonia nitrogen was deemed satisfactory in all cases. The period of 1.5 hours at 38° C. was used for the experiments reported in Tables IV and V and for results reported below.

TABLE V. RECOVERY OF AMMONIA NITROGEN FROM EGG YOLK CONTAINING VARYING ADDITIONS OF AMMONIUM SULFATE

(Results expressed as milligrams of ammonia nitrogen per 100 cc.)

No. of Detns.	Determined on Yolk Alone	Added to Yolk	Calculated Total	Actually Determined
4	3.47	1.81	5.28	5.23
4	2.49	1.81	4.30	4.40
4	3.47	3.38	6.85	6.76
4	2.49	3.38	5.87	5.80
4	3.47	4.73	8.20	8.23
4	2.49	4.73	7.22	7.39

In the procedure for egg white described above, the directions specify the use of liquid white. Firm white could also be used, but the liquid white is much easier to pipet and mix with the carbonate solution than the firm white and has the same percentage of ammonia nitrogen for the same egg. This is shown in Table VI, where the values for the three distinct layers of egg white for four eggs are given. All the results are within experimental error. In practice it was found satisfactory to slit the firm white envelope and pipet from the mixture of outside and inside liquid white.

TABLE VI. DISTRIBUTION OF AMMONIA NITROGEN IN EGG WHITE

(Results expressed as milligrams of ammonia nitrogen per 100 cc.)

Egg	Outside Liquid White	Firm White	Inside Liquid White
1	0.12	0.10	0.11
2	0.14	0.18	0.21
3	0.12	0.18	0.12
4	0.20	0.21	0.20

In a large number of eggs of similar history the ammonia nitrogen was determined for both white and yolk by the aëration and absorption methods. Both methods were not applied on the same samples. Reference to Table VII shows that in general there was satisfactory agreement between the values obtained by the two methods for both white and yolk on material of similar nature.

TABLE VII. COMPARISON OF RESULTS OF THE ANALYSIS OF EGGS BY AÉRATION AND ABSORPTION METHODS

Method	Material	No. of Samples	Ammonia Nitrogen Mg./100 cc.	Standard Deviation
Aëration	White	83	0.24	0.086
	Yolk	83	2.30	0.287
Absorption	White	16	0.35	0.137
	Yolk	301	2.41	0.280
	Mixed whole egg	6	0.87	0.003

Acknowledgment

The eggs used in this study were kindly supplied by the Poultry Section of the Experiment Station.

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Estimation of Oleomargarine in Ice Cream

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A method for determining the percentage of oleomargarine and butter fat in ice cream is given, which consists of a modified Rocse-Gottlieb extraction procedure combined with a modified Reichert-Meissl procedure. Formulas are derived for calculating the percentage of oleomargarine in the extracted fat, the fat being calculated in the usual manner.

THE lower price of oleomargarine as compared to butter fat at present has led some manufacturers of ice cream to substitute oleomargarine to some degree for butter fat. This may soon bring about serious consequences; it is illegal in many states and some investigators (3) have shown that ice cream made of oleomargarine is deficient in certain vitamins. It would seem obviously unfair to sell as ice cream a product that is not made of butter fat, but any ruling of fair trade competition must first have some basis for classification. This problem led the authors to work on a method for determining the relative amounts of oleomargarine and butter fat in ice cream with a reasonable degree of accuracy. The problem is more difficult than it first seemed. Modern homogenizing equipment has made microscopic examination and staining almost useless as a means of detecting oleomargarine, and refractive index and specific gravity gave no suitable quantitative data. The iodine value gave qualitative indication, but because of the diversity of oleomargarines on the market did not give quantitative confirmation. The Kirschner-Flanders (4) method did not give quantitative results when tried on the authors' samples. The usual Reichert-Meissl method (1) was also somewhat unsatisfactory and gave erratic results.

However, it was found that if the Rocse-Gottlieb extraction procedure and the Reichert-Meissl procedure were slightly modified, a precise method was obtained.

Experimental

APPARATUS. The usual apparatus for determining the fat percentage in butter was used (2).

REAGENTS. Oleomargarine was furnished by the Joseph Costa Co., Athens Ga., and had the following composition:

	%	%
Total fat		83
Oleic oil	34	
Neutral oil	34	
Cottonseed oil	15	
Moisture		12
Salt		3
Milk solids		2

Ammonium hydroxide, ethyl alcohol, diethyl ether, and petroleum ether as given by the method of the Association of Official Agricultural Chemist (2).

Sulfuric acid: 31.5 cc. of acid (sp. gr. 1.83) per liter.

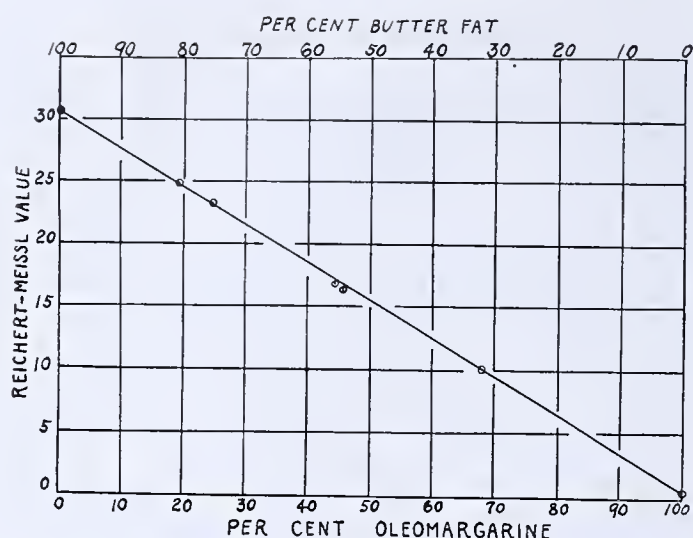


FIGURE 1. RELATION OF REICHERT-MEISSEL VALUE TO PERCENTAGE OF OLEOMARGARINE AND BUTTER FAT IN ICE CREAM

Procedure

EXTRACTION OF FAT FROM ICE CREAM. The ice cream is allowed to soften at room temperature. The fat soon separates and rises to the top, and the sample is then thoroughly mixed with an egg beater or other mechanical stirrer.

Aliquot portions of about 100 grams each are accurately weighed and the fat is extracted by using 12.5 cc. of ammonium hydroxide solution, 50 cc. of ethyl alcohol, 100 cc. of diethyl ether, and finally 100 cc. of petroleum ether. After the addition of each the mixture is thoroughly agitated in the separatory funnel for 30 seconds, and is then allowed to stand for 20 minutes, before separating the layers. As much as possible of the ether-fat solution is drawn off into a flask through a small, quick-acting filter. A second extraction, with 100 cc. of each ether, is necessary to insure complete removal of fat. The clear solution is drawn off through a small filter into the same flask; and the tip of the separatory funnel, the filter, and the funnel are washed with a few cubic centimeters of a mixture of equal parts of the two ethers, free from suspended water. The greatest portion of ether is distilled off, and the fat is dried in an oven at 90° C. to constant weight. The flask is weighed with a similar flask as a counterpoise. The fat is now ready for use, and can conveniently be handled at about 40° C. (A volume of about 5.5 cc. at this temperature weighs about 5 grams.) After samples have been taken from the flask, the fat is completely removed with petroleum ether. The weight of the dried flask with residue is deducted to obtain the weight of the fat.

Determination

Weigh out accurately a sample of about 5 grams of extracted fat in a tared glass vessel, add 10 cc. of ethyl alcohol and 2 cc. of sodium hydroxide solution, and saponify on a water bath (usually 1 hour).

Allow the flask to cool to room temperature after all alcohol has evaporated, taking care to prevent any loss of soap. The last traces of alcohol can be removed by waving the cool flask to and fro, mouth down. Dissolve the soap in 100 cc. of recently boiled distilled water and transfer to a 250-cc. distilling flask. Heat the flask up to 60° to 70° C. and add 40 cc. of sulfuric acid solution. Drop in a few pieces of pumice stone and connect to the condenser. Warm the flask until the fats separate as a clear layer, then continue the heating until 110 cc. of distillate have been collected in a graduated cylinder. The time of distillation should be between 28 and 32 minutes. Titrate a 100-cc. portion of the distillate with standard 0.1 N sodium hydroxide solution, using phenolphthalein as indicator. The Reichert-Meissl value is calculated from the usual formula.

$$\text{Reichert-Meissl value} = \frac{\text{cc. of NaOH} \times 1.1 \times 5}{\text{grams of sample}}$$

The procedure followed was to make up samples of ice cream varying from 100 to 0 per cent of butter fat and from 0 to 100 per cent of oleomargarine, and to analyze these according to the procedure outlined above. The results are given in Table I and Figure 1.

TABLE I. REICHERT-MEISSEL VALUES OF EXTRACTED FAT

Sample	Butter Fat %	Oleomargarine %	Reichert-Meissl Value
1	100.0	0.00	30.96
2	80.72	19.28	24.96
3	75.74	24.26	23.24
4	55.67	44.33	16.65
5	55.33	44.67	16.45
6	32.36	67.64	10.02
7	0.00	100.00	0.38

Duplicate determinations on butter fat varied ± 0.1 in the Reichert-Meissl value and ± 0.03 on oleomargarine duplicates. Taking 30.96 and 0.38 as reliable averages and the slope of the curve in Figure 1 as 0.31, it was possible to obtain a formula by substitutions in the classical equation for a straight line, $y = mx + b$, where m is the slope and b a constant.

Per cent of oleomargarine in fat =

$$\frac{30.96 - \text{Reichert-Meissl value}}{0.31} \quad (1)$$

Per cent of butter fat in fat = 100 - per cent of

$$\text{oleomargarine} = \frac{\text{Reichert-Meissl value} - 0.38}{0.31} \quad (2)$$

Since the variation in 0.38 is greater than that in 30.96, it is safer to subtract from 100 per cent to get butter fat.

To test this formula, samples of varying composition were prepared and submitted for analysis to Mr. Dunson who did not know their composition. The results are shown in Table II.

TABLE II. ANALYSES OF UNKNOWN SAMPLES

Sample	Reichert-Meissl Value	Calculated Percentage	Theoretical Percentage	Deviation
Oleomargarine 1	5.57	82.0	83.0	-1.0
Butter fat 1	5.57	18.0	17.0	+1.0
Oleomargarine 2	13.25	57.1	57.2	-0.1
Butter fat 2	13.25	42.9	42.8	+0.1
Oleomargarine 3	27.45	11.3	12.0	-0.7
Butter fat 3	27.45	88.7	88.9	+0.7

The percentage of fat may be calculated as usual.

$$\text{Per cent of fat in ice cream} = \frac{\text{grams of fat} \times 100}{\text{grams of ice cream}}$$

The composition of this fat is then calculated by Formula 1 and 2. The grams of oleomargarine and butter fat can be calculated easily and the percentage of oleomargarine in the original ice cream sample found by substituting grams of oleomargarine for grams of fat.

Discussion

Although this paper offers no new qualitative differentiation between butter fat and oleomargarine, it does offer a more exact quantitative determination, accomplished by standardizing the extraction method for ice cream, and by increasing the strength of the sulfuric acid in the usual Reichert-Meissl procedure. In this way more reliable results were obtained.

Only vanilla ice cream was used, but the method should apply to other flavors, particularly chocolate, caramel, and nut flavored ice cream.

The precision and accuracy are evident from the data presented.

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The Buffer Capacity of Tomato Juice

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THE capacity of various biological fluids to resist changes in hydrogen-ion concentration upon the addition of strong acid or base has been subject to much investigation, and has been studied quantitatively and developed mathematically by Van Slyke (6). Using the Van Slyke expression β or $\frac{dB}{dPH}$ expressing the relationship between the increment in gram equivalents of strong base added to the buffer solution and the resultant increment in pH, one of the authors measured β for solutions of gums (1), tincture of digitalis (2), carbohydrate of burdock (4), and oyster liquor (3).

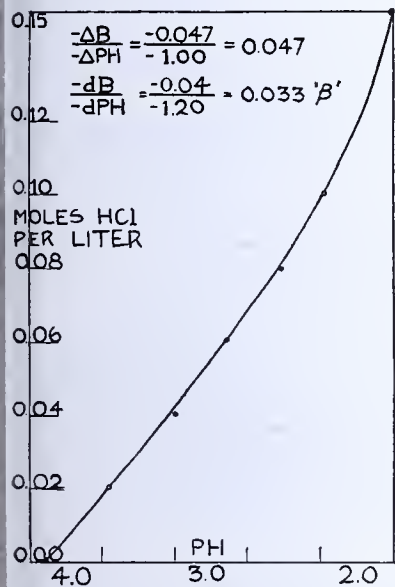


FIGURE 1. BUFFER CAPACITY OF TOMATO JUICE "ACID"

hydrochloric acid and sodium hydroxide solutions, respectively. The pH at $25^{\circ} \pm 1^{\circ} \text{C.}$ of the various solutions was determined with a Wilson-type (7) hydrogen electrode.

After the addition of acid to one sample and subsequent pH measurements, another portion was filtered and the serum treated in the same manner. The measurements made on the whole juice were practically identical with those made on the serum, indicating that the buffer capacity of the juice resides in the soluble constituents and not in the pulp.

The buffer capacities of the various serums to acid were studied individually and observed to be remarkably uniform. The juice prepared in this laboratory and the six commercial samples were practically identical in this respect. The buffer capacity of a composite sample is shown in Figure 1. The pH values of untreated juices obtained agree well with those determined by Mitchell (5) using the glass and hydrogen electrodes.

The addition of strongly dissociated alkali to the same tomato juice serums gave variable results, as shown by Table I.

TABLE I. EFFECT OF ADDITION OF ALKALI

No.	0.1 N NaOH Cc.	pH of Serum						Fresh
		No. 64	No. 65	No. 66	No. 67	No. 68	No. 69	
1	0.0	4.09	4.11	4.14	4.18	4.09	4.13	4.14
2	2.0	4.51	4.55	4.60	4.76	4.67	4.65	4.64
3	4.0	5.05	5.29	5.34	5.74	5.35	5.47	5.44
4	6.0	5.94	7.17	7.80	8.58	6.57	7.97	6.86
5	8.0	8.28	9.10	9.03	9.33	8.93	8.96	8.88
6	10.0	9.24	9.32	9.55	9.89	9.74	9.53	9.57

It occurred to the authors that it might prove of interest to measure the buffer capacity of tomato juice, and that this measurement might serve as a trustworthy index to added water or purposeful sophistication.

Experimental

Six standard grades of tomato juice, one juice prepared in this laboratory from sound, ripe tomatoes, and certain samples of tomato pulp were investigated. Samples of the juice (10 cc.) were treated with varying quantities of 0.1 N

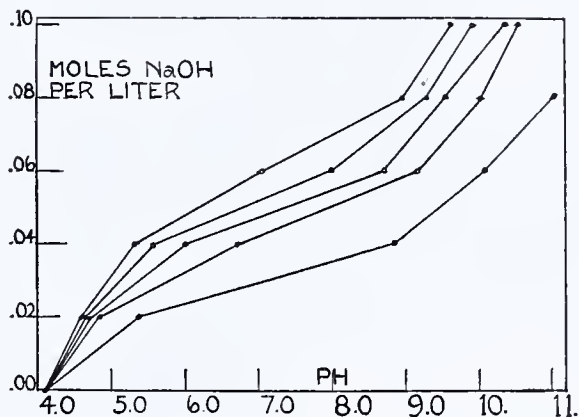


FIGURE 2. ACTION OF 0.1 N SODIUM HYDROXIDE ON TOMATO JUICE

As the buffer capacity of these samples varied so widely with respect to added alkali, it occurred to the authors to study the influence of added water on the buffer capacity of the serum with respect to added alkali. This was tested first on serum filtered from concentrated commercial pulp, and then after dilution of this with water. A marked diminution in the buffer capacity was observed when water was added.

Figure 2 shows the buffer capacity of the composite sample of serum upon the addition of strong alkali prior to and after the addition of varying quantities of water.

Other physical factors on the commercial juices were determined and are set forth in Table II.

TABLE II. COMMERCIAL JUICES

No.	Solids %	Ash %	NaCl %
64	6.08	1.22	0.84
65	6.44	1.05	0.66
66	6.80	1.13	0.76
67	6.40	1.20	0.80
68	6.52	1.08	0.70
69	5.39	0.90	0.63
Fresh	4.70	0.53	0.06

There seems to be little correlation between these data and the buffer capacity to alkalis. However, when these values are modified by sophistication in the form of added water the buffer capacity to alkali is markedly influenced. This condition did not obtain in respect to the addition of acid to the various serums. This is due in all probability to the citric acid content in the form of primary and secondary alkali citrates. The addition of alkali completely neutralizes the acid and thus destroys the naturally occurring buffer mixture. On the other hand, in the presence of added strongly dissociated acid, the buffer mixture is not markedly disturbed.

In order to represent graphically the effect of added water on the buffer capacity with respect to alkali, Figure 3 was constructed from the data in Figure 2. The ordinates designated

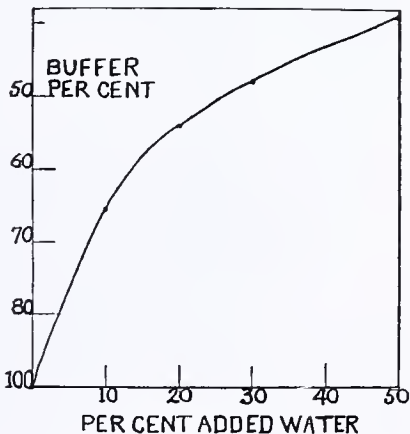


FIGURE 3. INFLUENCE OF SODIUM HYDROXIDE ON TOMATO JUICE WITH ADDED WATER

as "buffer per cent" were calculated as follows: The pH of the composite serum and the change caused by the addition of 0.06 mole of sodium hydroxide per liter were determined. The difference in pH between these two values was considered as the norm. With the sample diluted with water this difference successively increased. These increased differences divided into the norm and multiplied by 100 were designated as "buffer per cent." As these values diminish in magnitude they indicate decreased buffer capacity or, as a parallel, the quantity of added water.

In order to determine the possible application of this principle to the determination of added water, commercial samples were studied along with other juices pressed from sound, ripe tomatoes in this laboratory. The data are shown in Table III.

TABLE III. DETERMINATION OF ADDED WATER

No.	pH of Serum	pH of Serum		
		0.06 mole NaOH per liter	10 per cent water with 0.06 mole NaOH per liter	30 per cent water with 0.06 mole NaOH per liter
Commercial Samples				
1	4.11	8.60	9.09	9.85
2	4.20	8.56	9.07	9.95
3	4.18	8.60	9.03	9.73
4	4.07	8.67	9.06	9.75
5	4.13	8.15	8.60	9.56
6	4.05	6.46	8.00	9.00
7	4.03	6.59	8.11	9.12
8	4.09	8.15	8.75	9.45
9	4.12	7.95	8.75	9.57
10	4.17	8.32	8.84	9.43
11	4.22	8.86	9.40	10.23
Freshly Prepared Samples				
1	4.24	6.70	8.21	9.37
2	4.38	8.50	9.08	9.78
3	4.44	8.35	8.71	9.29
4	4.25	7.78	9.55	10.81
5	4.35	8.63	9.14	9.92

Table III confirms the finding of marked diminution in buffer capacity to alkali of both commercial and freshly

prepared tomato juices when water is added. Although the juices showed rather great variations in their buffer capacities, it seems reasonable to suspect that should the pH exceed 8.75 on a sample of tomato juice serum after the addition of 0.06 mole of sodium hydroxide per liter, water has been added to the extent of approximately 10 per cent. With a pH between 9.00 and 11.00, when treated with the same quantity of alkali, one might suspect the addition of approximately one-third volume of water.

Summary

The buffer capacity of six commercial samples of tomato juice has been measured with respect to strong acid. The Van Slyke β is 0.033. Added water does not markedly influence this value.

Tomato juices show considerable variation in their capacity to resist change in pH upon the addition of strong alkali. These values do not correlate well with normal differences found in total solids, salt content, ash, and refractive index.

The buffer capacity of the serum with respect to added alkali diminishes with increased added water.

It is possible to employ the measurement of buffer capacity corroboratively as means of detecting added water in tomato juice.

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The Hill Method for Solubility Determinations

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FOR determining the mutual solubilities of a pair of partially miscible liquids several direct experimental procedures are available. Alexejeff (1) described the well-known and widely used synthetic or cloud-point method as early as 1886, while in 1923 Hill (7) devised a very ingenious method based on phase rule considerations. In the Hill method the procedure is essentially as follows: Weighed amounts of the two liquids are introduced into a suitably graduated flask (a mixing cylinder, for example), shaken until equilibrium is reached, the phases allowed to separate, and the volumes of upper and lower layers read. The experiment is then repeated with a different ratio of starting materials. Now let

m_1, m_2 = weights of lighter and heavier liquids taken in the first experiment

m_3, m_4 = weights of lighter and heavier liquids taken in the second experiment

v_1, v_2 = volumes of upper and lower layers obtained in the first experiment

v_3, v_4 = volumes of upper and lower layers obtained in the second experiment

x_1 = grams of lighter liquid per cc. of upper layer (at saturation)

y_1 = grams of lighter liquid per cc. of lower layer (at saturation)

x_2 = grams of heavier liquid per cc. of upper layer (at saturation)

y_2 = grams of heavier liquid per cc. of lower layer (at saturation)

Then to determine the x 's and y 's we have

$$\begin{aligned} v_1x_1 + v_2y_1 &= m_1 & v_1x_2 + v_2y_2 &= m_2 \\ v_3x_1 + v_4y_1 &= m_3 & v_3x_2 + v_4y_2 &= m_4 \end{aligned}$$

These equations when solved yield

$$\begin{aligned} x_1 &= \frac{m_1v_4 - m_3v_2}{v_1v_4 - v_2v_3} & y_1 &= \frac{m_3v_1 - m_1v_3}{v_1v_4 - v_2v_3} \\ x_2 &= \frac{m_2v_4 - m_4v_2}{v_1v_4 - v_2v_3} & y_2 &= \frac{m_4v_1 - m_2v_3}{v_1v_4 - v_2v_3} \end{aligned}$$

As Hill has pointed out, this method is simple in application and has the advantage that besides yielding the solubility figures it also gives the densities of the two layers (as grams per cc.):

$$d_1 = x_1 + x_2 \quad d_2 = y_1 + y_2$$

One of the first questions to arise regarding this method was the proper choice of v_1, v_2, v_3 , and v_4 so as to obtain the greatest possible accuracy (9). Hill advocated the use of special equipment, so that a total volume of around 400 cc. could be used in each experiment, although he also pointed out that an ordinary 100-cc. mixing cylinder gave good results. For the proper choice of the ratio of v_1 to v_2 Hill and Malisoff (8) deduced that the materials should be taken so as to make $\frac{v_1}{v_2} = \frac{v_3}{v_4} = \frac{y_1}{x_1}$ in order to obtain the maximum accuracy in

determining x_1 , with similar expressions for the other variables. These conclusions were based on certain rather arbitrary assumptions which are not likely to prevail in practice. Briefly, these assumptions require no error in measuring v_2 and v_3 , and equal errors in sign and magnitude in measuring v_1 and v_4 . Because of the convenience of this solubility method it seems desirable to investigate this point further and determine suitable volume ratios when the errors in measuring the volumes are assumed independent of one another. Such a general choice for the v 's may be determined in the following manner:

It is assumed that the accuracy with which the liquids are weighed is sufficiently great so that errors from this or any other source can be neglected in comparison with errors in reading the volumes. In this case the m 's can be considered constants. Under these conditions, if v_1, v_2, v_3 , and v_4 denote the true volumes, then the changes in the x 's and y 's produced by small errors dv_1 , etc., in reading the volumes are given approximately by

$$\begin{aligned} dx_1 &= \frac{(m_3v_2v_4 - m_1v_4^2)dv_1 + (m_1v_3v_4 - m_3v_1v_4)dv_2 + (m_1v_2v_4 - m_3v_2^2)dv_3 + (m_3v_1v_2 - m_1v_2v_3)dv_4}{(v_1v_4 - v_2v_3)^2} \\ dx_2 &= \frac{(m_4v_2v_4 - m_2v_4^2)dv_1 + (m_2v_3v_4 - m_4v_1v_4)dv_2 + (m_2v_2v_4 - m_4v_2^2)dv_3 + (m_4v_1v_2 - m_2v_2v_3)dv_4}{(v_1v_4 - v_2v_3)^2} \\ dy_1 &= \frac{(m_1v_3v_4 - m_3v_2v_3)dv_1 + (m_3v_1v_3 - m_1v_3^2)dv_2 + (m_3v_1v_2 - m_1v_1v_4)dv_3 + (m_1v_1v_3 - m_3v_1^2)dv_4}{(v_1v_4 - v_2v_3)^2} \\ dy_2 &= \frac{(m_2v_3v_4 - m_4v_2v_3)dv_1 + (m_4v_1v_3 - m_2v_3^2)dv_2 + (m_4v_1v_2 - m_2v_1v_4)dv_3 + (m_2v_1v_3 - m_4v_1^2)dv_4}{(v_1v_4 - v_2v_3)^2} \end{aligned}$$

If finite values of the v 's could be found which would make all the parentheses in the numerators equal zero, and at the same time $v_1v_4 - v_2v_3 \neq 0$, then such a choice would be best in practice. Such values apparently do not exist. Thus, examining the coefficient of dv_1 in the expression for dx_1 , we would have $m_3v_2v_4 - m_1v_4^2 = 0$. Both v_2 and v_4 cannot equal zero, since in that case $v_1v_4 - v_2v_3 = 0$. Assuming $v_4 \neq 0$, this condition becomes $m_3v_2 - m_1v_4 = 0$. If absolute accuracy were secured in the experiment then

$$v_4 = \frac{m_4x_1 - m_3x_2}{x_1y_2 - x_2y_1} \quad v_2 = \frac{m_2x_1 - m_1x_2}{x_1y_2 - x_2y_1}$$

Substituting these values we have

$$\frac{x_1(m_1m_4 - m_2m_3)}{x_1y_2 - x_2y_1} = 0 \text{ or } \frac{m_1}{m_3} = \frac{m_2}{m_4}$$

Hence the requirement that the coefficient of dv_1 be zero is satisfied only under conditions such that the original equations do not define the x 's and y 's uniquely. (The previously cited conclusions of Hill and Malisoff may be derived easily from the foregoing equations. For example, it is necessary to assume in the expression for dx_1 that $v_2 = v_3, v_1 = v_4 = kv_2, dv_2 = dv_3 = 0, dv_1 = dv_4$, and then set the numerator of the fraction equal to zero.)

While it is impossible to choose the conditions such that the dx 's and dy 's are zero for all values of the dv 's, nevertheless a suitable choice of the v 's may suffice to make the dx 's and dy 's relatively small. Inasmuch as the dx 's and dy 's are expressed as fractions, and all the fractions have the same denominator, it seems plausible that if the v 's are chosen so as to make this denominator a maximum the most suitable general choice of the v 's will have been made. This may be accomplished by making both v_1 and v_4 (or v_2 and v_3) as small as is experimentally possible, and the other volumes correspondingly large. Under these conditions, as v_1 and v_4 both approach zero, the errors introduced by small errors in reading the volumes become roughly the following:

$$\begin{aligned} dx_1 &= -\frac{m_3}{v_3^2} dv_3 - \frac{m_1}{v_2v_3} dv_4 \\ dx_2 &= -\frac{m_2}{v_2v_3} dv_4 - \frac{m_4}{v_3^2} dv_3 \\ dy_1 &= -\frac{m_3}{v_2v_3} dv_1 - \frac{m_1}{v_3^2} dv_2 \\ dy_2 &= -\frac{m_2}{v_2^2} dv_2 - \frac{m_4}{v_2v_3} dv_1 \end{aligned}$$

Unless the liquids are fairly soluble in each other, the coefficient of the last term in each of the above expressions is small in comparison to the preceding one.

Granting this choice of volumes to be the most suitable, it is evident that the solubility bottles should be such as to permit accurate reading of both the total volume and the small volume of upper or lower layer as the case may be. One such type of bottle is the so-called oil centrifuge bottle shown in Figure 1. These bottles hold approximately 50 cc., and have their necks graduated directly to 0.05 cc. over a 5-cc. volume,

the distance between graduations being approximately 1.3 mm. Consequently, by calibrating the graduations it is possible to read both the total volume and a small upper layer volume to about 0.025 cc. For the other measurement, involving a small lower layer, the standard centrifuge tubes with tapered bottoms might be used,

except that they afford poor accuracy in the total volume determination. Consequently it seems best to use the same oil centrifuge bottle, with the modification of introducing about 0.5 cc. of mercury originally. As before, the total volume is readily secured, while by inverting the tube the volume of lower layer may be determined, since the mercury seals off the uncalibrated portion of the tube. Another similar type of bottle, known as the Babcock bottle, has a slightly smaller neck which is graduated for a volume of 1.8 cc. in 0.02-cc. divisions. A special bottle may obviously be constructed having a small graduated well in the bottom, which should be very suitable for this type of measurement.

The advantages of using this type of bottle are (1) the bottle is a standard, inexpensive article of manufacture; (2) relatively small quantities of liquid are required for fair precision, and (3) the bottle may be readily centrifuged, thus giving a quick and complete separation of the phases. With the larger, specially built flasks centrifuging is virtually impossible and phase separation often difficult.

To give an idea of the accuracy which can be attained by the use of this type of equipment the preceding set of equations may be evaluated for different choices of the variables. Using the oil bottle which is graduated directly to 0.05 cc., the volumes of the phases should be accurate to within 0.025 cc., while the larger phase will be about 50 cc., and the smaller about 1 cc. in volume. Assuming values for x_1, y_1, x_2 , and y_2 of 0.6, 0.2, 0.2, and 0.7, respectively, an error in each volume of 0.025 cc. can introduce an error of approximately 0.0004 in x_1 and y_1 , and 0.0005 in x_2 and y_2 . Consequently the solubility percentages obtained should not differ from the true values by over 0.1 per cent in absolute value, and the density should be accurate to within 0.001. If the individual

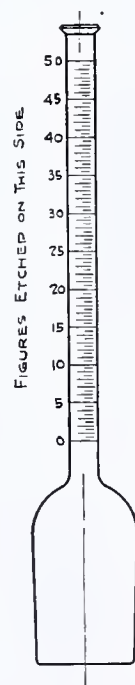


FIGURE 1.
OIL CEN-
TRIFUGE
BOTTLE

volumes are in error by as much as 0.05 cc., then the solubility figures can differ from the true values by 0.2 per cent and the density be incorrect by 0.002. This assumes, of course, that the starting materials are pure, that there are no handling losses, and that equilibrium is reached, so that only errors in measurement need be considered. This degree of accuracy is sufficient for many purposes, and consequently this method can be used conveniently in these cases.

TABLE I. WATER SOLUBILITY MEASUREMENTS

Substance	Water Saturated with Substance at 20° C.		Substance Saturated with Water at 20° C.	
	% A	d_4^{20}	% A	d_4^{20}
Secondary butyl alcohol ^a	18.5	0.971	64.4	0.880
Methyl ethyl ketone ^b	26.7	0.962	87.9	0.836
Methyl <i>tert</i> -butyl ether ^c	4.8	0.990	98.5	0.745
Methyl <i>tert</i> -amyl ether ^d	1.25	0.995	99.3	0.771
Chloroform ^e	0.8	1.001	99.8	1.486

^a Clough and Johns give the values 17.85, 0.9732, 64.17, 0.8797 (3). Earlier work by Timmermans gives percentages of 20.2 and 63.8.

^b A plot of Marshall's data gives methyl ethyl ketone saturated with water as 88.0 per cent ketone (10).

^c Bennet and Philip give percentages of 5.83 and 97.46. Their sample of ether was less pure than that used here, boiling lower and having a higher density, indicating the probable presence of alcohol (2).

^d Determinations by the synthetic method have given percentages of 1.15 and 99.4 (4).

^e Gross and Saylor, using an interferometer method, give values for water saturated with chloroform of 0.77 per cent at 30° C. and 0.84 per cent at 15° C. (6). Gibby and Hall by the synthetic method found chloroform saturated with water to contain 99.93 per cent of chloroform (5).

As examples of the results obtained using the apparatus described above, the data in Table I are presented. They

represent water solubility measurements for several types of organic compounds ranging from a fairly soluble material such as secondary butyl alcohol to a fairly insoluble one such as chloroform. Wherever available the corresponding data obtained by other methods are given for comparison. The agreement is generally satisfactory, and where there are discrepancies these seem to be due in part to differences in the purity of the starting materials.

Summary

The Hill method for solubility determinations has been investigated and a suitable general choice determined for the volume ratios employed. A simple and inexpensive apparatus is described for carrying out the determinations and experimental results obtained with this apparatus are given.

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A Manipulator for Glass Blowing

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AS IT IS extremely awkward and tiring to manipulate large and bulky pieces of glass in glass blowing, it has been customary to employ some sort of rest for the object being worked. After some experience of this kind the author has designed and constructed the device illustrated. While the idea is not new, the design is and has been found ideally suited for handling any type of apparatus ordinarily constructed in the laboratory. This manipulator offers extreme flexibility in use, due to its wide range of adjustment.

The actual working parts are mounted on a solid brass rod, *C*, with a slotted hinge joint, *E*, which permits adjustment at any angle to the horizontal. This rod works in a hollow brass tube,

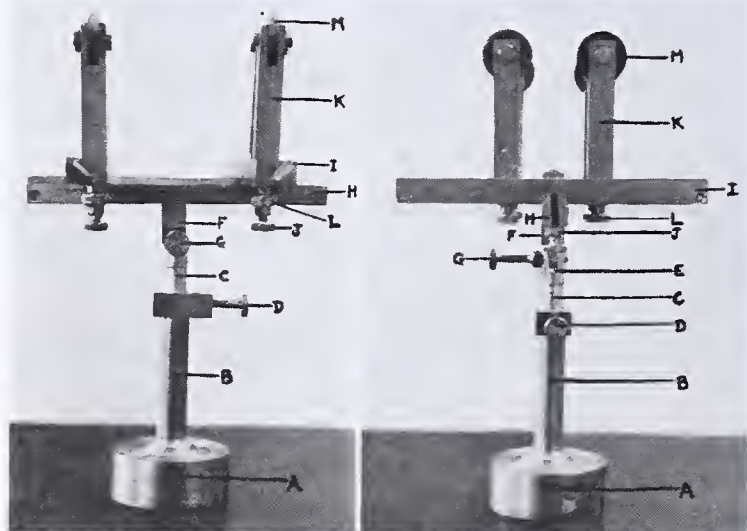
B, with a set screw, *D*, so that it may be adjusted for height. The hollow rod is mounted in a heavy base, *A*. In the author's instrument the hollow tube is 11 cm. high, but this, of course, depends upon the size of the blast lamp being used. The solid brass rod, which should fit snugly into the hollow one, is 12.5 cm. from the bottom to the axis of the hinge joint, which is made by slotting the solid rod and rounding off the top surface. A 2.5-cm. piece of brass, *F*, 13 mm. square, is worked down to fit the slot and the two pieces are then drilled and tapped to take a set screw, *G*. To the top of this square piece of brass another piece of brass, *H*, 13 mm. square and 15 cm. long, is joined by two screws in the center, to form a runner for the two carriages, *I*. It is grooved all the way through except for about 2 cm. in the center where the screws attaching it to the upright pass through. It was necessary to place a screw at each end to keep it from warping. The top surface is milled down at an angle to fit into a cross groove in the bottom of each carriage.

The carriages, made of two 15-cm. pieces of brass 13 × 20 mm. are held on the runner by set screws, *J*. They are grooved all the way through except for 1.5 cm. in the center and are fastened at each end with a screw to prevent warping. The carriages are then milled to carry the uprights, *K*, which are made of 7.5-cm. pieces of brass 13 mm. square.

The bottoms of the uprights are milled to fit snugly into the carriage groove where they are held in place by set screws, *L*. The tops of the uprights are slotted to carry Bakelite or fiber wheels, *M*, with a diameter of 2.5 or 3 cm. These wheels, which carry the glass, should be free to rotate easily.

When constructed in this manner it is possible to carry any diameter of tubing. The wheels on which the tubing rests permit it to be rotated easily and at any desired speed without tiring the hand by supporting. The carriages may be set close together to carry short pieces of glass or far apart to support longer and heavier pieces. The whole instrument may be tilted and used at any angle desired.

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A New Reagent for Potassium

I. Qualitative

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THE solubility of the disodium salt of 2,4-dinitro-1-naphthol-7-sulfonic acid as compared with the dipotassium salt has suggested its use as a reagent for the detection of potassium. The present investigation is a study of its applicability for this purpose. Both the disodium and dipotassium salts are known as naphthol yellow S, but the product usually found on the market is the disodium salt and is the compound designated in this paper as naphthol yellow S.

Naphthol yellow S reacts readily with potassium to form a very bulky, flocculent, orange-yellow precipitate. The rate at which precipitation occurs is dependent upon the concentration of the reagent and of potassium.

General Procedure

To determine the sensitiveness of naphthol yellow S as a qualitative reagent for potassium, it was dissolved in water, and concentrations of 5 and 2 per cent and a solution saturated at room temperature were used. The 5 and 2 per cent solutions were prepared by heating 5 and 2 grams, respectively, in 100 ml. of water until all the naphthol yellow S was dissolved and then keeping these solutions at a temperature of 50° C. or more. This was necessary since the concentration of a solution saturated at room temperature is less than 1.5 per cent. In each series of experiments the same volume of test solution was used with varying concentrations of potassium as potassium sulfate. To each was added the same volume of reagent of a given concentration, and the mixtures, after shaking, were allowed to stand at room temperature.

SENSITIVENESS OF NAPHTHOL YELLOW S AS A TEST FOR POTASSIUM. The following experiments show the sensitiveness of the reagent in the absence of all other cations: (1) three milliliters of a 5 per cent solution of the reagent were added to 10 ml. of test solutions of various concentrations of potassium. (2) This was repeated using a 2 per cent solution. (3) Five milliliters of a solution of the reagent saturated at room temperature were added to 1 ml. of test solution of various concentrations of potassium. The results are given in Table I.

TABLE I. SENSITIVENESS OF NAPHTHOL YELLOW S AS A TEST FOR POTASSIUM

Experiment	Potassium in Reaction Mixture	Time Elapsed before Appearance of Precipitate		Saturated solution of reagent
	Mg./ml.	5 per cent reagent	2 per cent reagent	
		Min.	Min.	Min.
1	7.87	0	1	
2	3.94	Less than 1	4	
3	3.15	1	10	
4	2.36	2	15	
5	1.57	3	30	9
6	0.79	8	65	40
7	0.39	16	4 hours	5 hours
8	0.03	More than 6.5 hours	No ppt. formed	No ppt. formed
9	0.00	More than 6.5 hours	No ppt. formed	No ppt. formed

Using a 5 per cent solution, a blank test should be run, since this concentrated reagent crystallizes out on long standing. To avoid the necessity of running a blank, a more dilute solution was used. The reaction of a solution saturated at room temperature was too slow for practical use.

The use of a 2 per cent solution is recommended, since it obviates the necessity of running a blank, although its sensitivity is less than the 5 per cent solution, as shown by the increase in time required to cause precipitation. Using a 5 per cent solution, the bulk of the precipitate and the length

of time required for its formation will enable one to differentiate between the blank and the potassium precipitate where the amount of potassium is 0.4 mg. or more per ml. of reaction mixture.

EFFECT OF SODIUM IONS. Ten milliliters of sodium chloride solution containing 0.1030 gram of sodium were mixed with 10 ml. of potassium sulfate solution and 6 ml. of naphthol yellow S were added. The concentrations of the potassium sulfate solutions were varied and all other factors kept constant. The results, compared to other solutions containing only the reagent and potassium sulfate of the same concentrations, are shown in Table II.

TABLE II. EFFECT OF SODIUM ON DETECTION OF POTASSIUM BY NAPHTHOL YELLOW S

Experiment	Potassium in Reaction Mixture	Sodium in Reaction Mixture	Ratio of Na to K	Time elapsed before Appearance of Precipitate
	Mg./ml.	Mg./ml.		Min.
1A	3.93	3.96	1:1	1
1B	3.94	Less than 1
2A	1.96	3.96	2:1	4
3A	1.57	3.96	2.52:1	8
3B	1.57	2
4A	1.18	3.96	3.35:1	15
5A	0.79	3.96	5.03:1	30
5B	0.79	8
6A	0.39	3.96	10:1	65
6B	0.39	16
7A	0.19	3.96	20:1	Less than 24 hours
8A	0.02	3.96	26.4:1	No ppt. formed
9B	..	3.96	No ppt. formed

The amount of precipitate obtained in the A and B series was much the same, but there was a marked difference in physical appearance. The solution containing sodium produced an orange precipitate of a finer texture, which settled much more readily. The most noticeable effect of the sodium was that about four times as long was required to produce a precipitate. Increasing the ratio of sodium to potassium appeared to have little or no effect.

OTHER INTERFERENCE. Ten milliliters of test solution containing 80 mg. of one of the cations commonly associated with potassium and 3 ml. of a 2 per cent solution of the reagent were mixed and set aside at room temperature. The cations tested were the chlorides of lithium, sodium, and ammonium, and sulfate of magnesium. At the end of 24 hours no precipitate was formed, but the test containing ammonium gave a slight precipitate in 48 hours.

Rubidium and cesium, the other two alkali metals associated with potassium, are so infrequently encountered that interference from these elements is not likely to occur.

DETAILS OF PROCEDURE. To 10 ml. of the aqueous solution to be tested, containing only the soluble group, add 3 ml. of a 2 per cent solution of naphthol yellow S and set aside at room temperature. The appearance of a precipitate in 65 minutes or less will indicate the presence of 0.79 mg. of potassium or more per ml. of reaction mixture. As an alternative procedure, 3 ml. of a 5 per cent solution of the reagent may be used, with a blank test run under the same conditions. The appearance of a precipitate in 20 minutes or less at room temperature will indicate the presence of 0.39 mg. or more of potassium per ml. of reaction mixture.

Discussion

The salts of potassium are very soluble in water and so the number of reagents that will detect 1 part of potassium in

2500 parts of solution are comparatively few (1). They are phosphotungstic acid, sodium 6-chloro-5-nitro-*m*-toluene sulfonate, and sodium cobaltinitrite.

Phosphotungstic acid easily forms supersaturated solutions and so is unreliable. The other two react readily with ammonium, which necessitates its removal before the test is made. Sodium cobaltinitrite, the most sensitive reagent for potassium, easily decomposes and as such is useless for the test.

Naphthol yellow S is a stable reagent which will detect at least 1 part of potassium in 2500 parts of solution and the presence of sodium and ammonium ions does not interfere with the test.

Summary

A 2 per cent solution of naphthol yellow S, used in the ratio of 3 ml. of reagent to 10 ml. of test solution, is recommended for general use as a test for potassium.

For test solutions containing less than 0.79 mg. of potassium per ml., 3 ml. of a 5 per cent solution of the reagent to 10 ml. of test solution should be used. This necessitates running a blank.

The reagent will detect 1 part of potassium in 2500 parts of solution.

The presence of sodium does not interfere with the test but does increase the length of time before precipitation occurs.

Ammonium and other cations commonly associated with potassium do not interfere with the test.

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Action of 4-Nitrocatechol as a Titration Indicator

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BENEDIKT (1), who first mentioned 4-nitrocatechol, obtained it by the action of dilute sulfuric acid upon a dilute solution of a mixture of catechol and potassium nitrite. He stated that this substance was yellow under acid conditions and red under alkaline conditions, and should be an excellent indicator for acid-base titrations.

The object of this investigation was to ascertain if 4-nitrocatechol could be used in titrations and the type of titrations in which it could be employed.

PREPARATION OF REAGENTS. The 4-nitrocatechol was prepared by the method of Benedikt (1), and was further purified by distilling the solid in a vacuum of 2 mm. and collecting the portion which came over between 190° and 210° C. The distillate was dissolved in ether and filtered, and the ether allowed to evaporate. A light yellow product which melted at 174° C. was obtained.

Approximately 0.1 *N* solutions of hydrochloric, nitric, acetic, and oxalic acids, sodium hydroxide, sodium carbonate, and ammonium hydroxide were prepared.

COLOR CHANGES AND CONSTANTS OF INDICATOR. The indicator changes from very light straw color under distinctly acid conditions to lemon yellow and finally to red as alkali is added to a solution containing it. The change from straw color to lemon yellow is sharp and that from lemon yellow to red gradual.

The ionization constants were determined by using a Bausch and Lomb hydrogen-ion colorimeter and checking the pH of the buffer solutions employed by means of a Queen potentiometer, using the customary hydrogen-calomel combination. The pK_a for the first hydrogen was found to be 6.56 and for the second hydrogen 11.33 at 25° C. Gilbert, Laxton, and Prideaux (2) found the pK_a for the first hydrogen to be 5.56 and for the second hydrogen 10.96 by employing a similar method.

The ranges of the color changes were obtained by observing the colors produced in a series of buffer solutions. The pH range for the change from straw color to red was found to be 3.92 to 10.57, and from straw color to lemon yellow 3.92 to 6.34 at 25° C.

TITRATIONS. Titrations of acids with bases were made by using the appropriate indicator in each case. These were compared with similar titrations made by employing a 1 per cent aqueous solution of 4-nitrocatechol as the indicator. The color change used to designate the end point when this

indicator was employed was from straw color to lemon yellow. In the case of sodium carbonate the salt was treated with a slight excess of hydrochloric acid, boiled to free the solution from carbonic acid, and then back-titrated with sodium hydroxide solution when the 4-nitrocatechol was used as the indicator.

TABLE I. TITRATIONS OF ACIDS WITH BASES^a

Acid Ml.	Base Ml.	Ratio (Acid/Base)	Indicator
HCl	NaOH		
25.0	20.8	1.20	Methyl orange
25.3	21.2	1.19	Phenolphthalein
26.68	22.22	1.20	4-Nitrocatechol
HCl	NH ₄ OH		
25.06	25.44	0.985	Methyl orange
25.02	25.34	0.987	4-Nitrocatechol
HNO ₃	NaOH		
25.0	20.69	1.208	Phenolphthalein
25.0	20.60	1.214	4-Nitrocatechol

^a The values are the averages of several titrations.

Discussion

The authors feel that the differences between the constants which they have obtained and those obtained by Gilbert, Laxton, and Prideaux (2) were due to a difference in the purity of the two compounds. Their compound was described as being light brown and melting at 173° C., whereas the authors' compound was light yellow and melted at 174° C., and the product obtained before vacuum distillation was light brown. During the distillation a light brown product came over first and then a yellow distillate which was collected and used in the authors' study.

The 4-nitrocatechol is useful for titrations of strong acids with strong bases and strong acids with weak bases, but cannot be used in titrations of weak acids. A strong oxidizing acid like nitric did not affect its operation, but on the other hand it did not function well in a solution containing much carbon dioxide.

Summary

A 1 per cent aqueous solution of 4-nitrocatechol has been employed for titrations of nitric acid with sodium hydroxide, hydrochloric acid with ammonium hydroxide, hydrochloric acid with sodium hydroxide, and sodium carbonate with hydrochloric acid.

The action of the indicator is affected by carbon dioxide, but not by a strong oxidizing acid like nitric.

The indicator changes from a very light straw color under acid conditions to lemon yellow and finally red as alkali is added, the first change being sharp and the second gradual.

The pH range for the change from straw color to red was found to be 3.92 to 10.57 and for the change from straw color to lemon yellow 3.92 to 6.34 at 25° C.

The pK_a for the first hydrogen was found to be 6.56 and for the second hydrogen 11.33 at 25° C.

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Determination of Small Amounts of Potassium by Means of Silver Cobaltinitrite

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THE determination of small quantities of potassium is of prime importance in the study of biological fluids, soil extracts, and fresh waters. Because of incomplete precipitation when there is less than 0.100 mg. of potassium per ml., the widely used method based on precipitation with sodium cobaltinitrite leaves much to be desired (7, 11). Even when the potassium concentration is 0.150 mg. per ml. or more, satisfactory results are obtained only because of compensation of errors of rather large magnitude (7, 13). Taylor (14) has shown that the sensitivity of the method is increased with an alcoholic precipitation medium. Reported below are preliminary experiments with the sodium cobaltinitrite reagent establishing the lower limit of each of these procedures. From these data it is apparent that neither method possesses the sensitivity necessary for the direct determination of extremely small amounts of potassium, such as are found in most lake and river waters. Since concentration by evaporation in quartz or platinum is time-consuming and requires expensive equipment, a direct determination would be most desirable for water analysis. The silver cobaltinitrite method of Breh and Gaebler (2) appeared to offer the most promise for such a direct determination. Using a modification of this method, smaller amounts of potassium than reported elsewhere in the literature have been determined.

Colorimetric Determination of Nitrite

Heretofore the most sensitive method for the determination of potassium has been based upon the precipitation of $(\text{Na}, \text{K})_3\text{Co}(\text{NO}_2)_6$ with subsequent determination of the cobalt or nitrite colorimetrically (7). The extremely sensitive Greiss method has been extensively used for the colorimetric estimation of the nitrite content of this precipitate (5).

PROCEDURE. A solution containing 0.0005 to 0.0050 mg. of NO_2 (1), which is equivalent to approximately 0.0001 to 0.0010 mg. of potassium, respectively, was diluted to 50 ml. in a Nessler tube, and was treated with a mixture of 2 ml. of sulfanilic acid and 1 ml. of 1-naphthylamine (1). Comparison was made with standards after the color had developed 20 minutes. To determine 0.005 to 0.100 mg. of NO_2 the solution was diluted to 100 ml., the color developed and the comparison with standards made in a Klett colorimeter.

OBSERVATIONS ON THE COLORIMETRIC TECHNIC. From investigations of the colorimetric technic, the authors draw the following conclusions: First, to obtain strictly reproducible results the sulfanilic acid and 1-naphthylamine should first be mixed and then added to the nitrite solution. When the Greiss reagents are added separately, the color is, within certain limits, more intense the longer the time interval between the addition of the sulfanilic acid and the 1-naphthylamine. This observation has been noted by others (7, 9), though most investigators fail to heed this precaution. The mixture of reagents was found to be stable for at least 2 weeks in the absence of light (9). Secondly,

confirming the work of Taylor (14) it was found that the use of a 10 per cent acetic acid medium prevents the formation of a reddish brown precipitate with large quantities of nitrite. Furthermore, when acetic acid and sodium acetate are used, they must be present in the same concentration in both standard and unknown (16). Thirdly, Beer's law is valid over a range of 0.0001 to 0.0010 mg. of NO_2 per ml. of solution, which is equivalent to 0.00002 to 0.00020 mg. of potassium per ml.

Determination of Potassium with Sodium Cobaltinitrite Reagent

For the purpose of ascertaining the sensitivity of the sodium cobaltinitrite reagent, the authors employed a modification of the method (15) which Tischer had claimed to be more sensitive than previous methods. More recent work indicates that the Kramer-Tisdall (6) reagent may be somewhat more sensitive, though surely not less than 0.025 mg. of potassium per ml. can be determined with accuracy (12).

In the present investigation the modifications of the Tischer method were: (1) the precipitate was separated by centrifuging; (2) the precipitate was dissolved in 0.1 *N* sodium hydroxide; and (3) the nitrite was determined with the Greiss reagents. The first two modifications were recommended by Lewis and Marmoy (7), while Herzner (5) showed that the Greiss reagents may be used satisfactorily for the determination of nitrite.

The results with this modified procedure were corrected for a blank which ranged from 0.00002 to 0.0007 mg. of potassium. No precipitation was observed when the potassium concentration was less than 0.040 mg. per ml., although a precipitate of $(\text{Na}, \text{K})_3\text{Co}(\text{NO}_2)_6$ containing 0.001 mg. of potassium may be seen easily in the centrifuge tube. Moreover, seeding the reagent just before use did not increase the sensitivity of the reagent. It was found that a minimum of 0.120 mg. of potassium per ml. may be determined with accuracy when calculating the potassium from a potassium-nitrite factor based on the $\text{NaK}_2\text{Co}(\text{NO}_2)_6$ formula as Tischer did, whereas somewhat less than 0.080 mg. may be estimated quantitatively if potassium standards are carried through simultaneously with the unknowns for the colorimetric comparison.

Taylor (14) obtained an increased sensitivity with the sodium cobaltinitrite reagent by the use of a precipitation medium containing about 30 volume-per cent ethyl alcohol. Recently Lohse (8) reported results for Taylor's procedure when the precipitation was made at low temperatures. However, the smallest concentration of potassium reported by Lohse was 0.100 mg. per ml. and, other than this, the effect of cooling upon the sensitivity was not given. In Table I the sensitivity with the Taylor procedure is given for both room temperature and 4° to 6° C. The colorimetric com-

parison and estimation were made against standard potassium solutions treated simultaneously with the unknowns.

TABLE I. POTASSIUM RECOVERY WITH TAYLOR'S PROCEDURE

Potassium at Room Temperature			Potassium at 4° to 6° C.		
Present	Found	Difference	Present	Found	Difference
Mg./ml.	Mg./ml.	Mg./ml.	Mg./ml.	Mg./ml.	Mg./ml.
			0.0020	0.0000	-0.0020
				0.0000	-0.0020
				0.0000	-0.0020
0.0030	0.0000	-0.0030	0.0030	0.0037	+0.0007
	0.0000	-0.0030		0.0019	-0.0011
	0.0000	-0.0030		0.0030	0.0000
0.0060	0.0060	0.0000	0.0060	0.0056	-0.0004
	0.0065	+0.0005		0.0061	+0.0001
	0.0060	0.0000		0.0060	0.0000
0.0120	0.0121	+0.0001	0.0100	0.0100	0.0000
	0.0120	0.0000		0.0091	-0.0009
	0.0120	0.0000		0.0112	+0.0012
0.0300	0.0300	0.0000	0.0200	0.0201	+0.0001
	0.0290	-0.0010		0.0200	0.0000
	0.0300	0.0000		0.0190	-0.0010

On the basis of these results it can be stated that cooling enables the determination of smaller amounts of potassium. At 4° to 6° C., 0.0030 mg. of potassium was determined with fair accuracy while at room temperature no precipitate was formed at all. Furthermore, a comparison of the sensitivity of this method with that of the Tischer method confirms the conclusions of Taylor that an alcoholic precipitation medium increases the sensitivity of the procedure.

Formulas ranging from $\text{KNa}_2\text{Co}(\text{NO}_2)_6$ to $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ have been reported as representing the composition of the precipitate, but the composition is now generally agreed to be a mixture of these two forms whose ratio varies, depending upon the conditions of precipitation, and is well represented by the formula $(\text{K},\text{Na})_3\text{Co}(\text{NO}_2)_6$. However, with careful regulation of conditions the composition is fairly reproducible from one time to another. The formula which best represented the product in the above determinations was calculated to be $\text{K}_{1.35}\text{Na}_{1.65}\text{Co}(\text{NO}_2)_6$, assuming that all the potassium was precipitated. Using standard nitrite solutions for the colorimetric comparison, and a potassium-nitrite factor based on the latter formula, the weight of $(\text{K},\text{Na})_3\text{Co}(\text{NO}_2)_6$ precipitated is readily calculated. When this was done the increased recovery of potassium at the lower temperature of precipitation was evident. By this method not less than 0.030 mg. of potassium could be accurately estimated at room temperature while as little as 0.006 mg. of potassium per ml. could be determined at the lower temperature.

Precipitation with Silver Cobaltinitrite

Silver cobaltinitrite reagent is the most sensitive of all precipitants of potassium (3, 10), yet, with the exception of Breh and Gaebler's (2) investigation in blood serum, there have been no attempts to apply this reagent to quantitative work. They stated that, with their procedure, it is possible to precipitate as little as 0.083 mg. of potassium from 5 ml. of blood serum filtrate and by using a calibration curve to obtain the results with an accuracy of 3 to 5 per cent.

Although it has been reported (3) that silver potassium cobaltinitrite has a pronounced tendency to become colloidal in the absence of alcohol and electrolytes, Breh and Gaebler used distilled water as the wash liquor. In the following experiments acetone was the wash solution; alcohol was also tried but acetone was superior. An all-glass wash bottle was essential for use with either alcohol or acetone, as unsaturated compounds were often leached from the rubber connections with subsequent reduction of the silver in the precipitate.

STANDARDS AND REAGENTS. In all instances the reagents were prepared from purified C. P. chemicals.

Alcohol and acetone were of such purity that neither gave a perceptible precipitate when treated with silver nitrate, allowed to stand for 3 hours at room temperature, and then centrifuged.

Silver cobaltinitrite reagent containing 1.0 per cent of silver nitrate was prepared by dissolving 25 grams of sodium cobaltinitrite in 150 ml. of sodium nitrite solution, containing 50 grams of sodium nitrite, and adding with stirring 5 ml. of silver nitrate solution, containing 2.0 grams of silver nitrate. The solution was diluted to 200 ml., 2 ml. of glacial acetic acid were added, and air was passed through the cold solution for 5 minutes. After standing for about 12 hours at 4° to 6° C., the reagent was filtered through a No. 42 Whatman filter paper.

Fresh reagent was prepared at least once every 2 weeks and was preserved at 4° to 6° C. when not in use. Just before use a portion was centrifuged and the supernatant solution used for precipitation of the potassium.

A stock solution of potassium sulfate was prepared to contain 1.000 mg. of potassium per ml. Standard solutions were prepared by proper dilution.

Synthetic hard water, potassium-free, had the following composition in parts per million: Ca^{++} , 195; Mg^{++} , 53.3; Na^+ , 780; Fe^{+++} , 35; SiO_3^{--} , 150; Cl^- , 1080; SO_4^{--} , 582. The solution was 0.17 *N* in respect to acetic acid.

PROCEDURE. One milliliter of a standard potassium solution was measured into a 15-ml. centrifuge tube and 1.00 ml. of the silver cobaltinitrite added. The precipitate and solution were allowed to stand for 3 hours and then centrifuged at 3000 r. p. m. for 15 minutes. The supernatant liquid was carefully removed through a siphon. The first washing was made with 5 ml. of water, the second with the same volume of 60 volume-per cent acetone, and subsequent washings with the same volume of 99.5 per cent acetone. After centrifuging 5 to 10 minutes, the wash liquid was removed by siphoning. The precipitate was finally dissolved in 1 ml. of 0.1 *N* sodium hydroxide. Solution was quickly completed by immersing the tube in a boiling water bath for 10 to 15 minutes. The Greiss reagents were added and the colorimetric comparison was made against potassium standards that had been treated identically. When the amount of potassium was believed to be under 0.001 mg. the comparison was made in a colorimeter, using an aliquot containing 0.001 to 0.020 mg. of potassium.

Following this procedure, known amounts of potassium in distilled water were precipitated both at room temperature and at 0° C. to determine the sensitivity and the accuracy of the method at the two temperatures. These results are shown in Table II.

TABLE II. POTASSIUM RECOVERY WITH THE SILVER COBALTNITRITE REAGENT

Potassium at Room Temperature			Potassium at 0° C.		
Present	Found	Difference	Present	Found	Difference
Mg./ml.	Mg./ml.	Mg./ml.	Mg./ml.	Mg./ml.	Mg./ml.
			0.0010	0.0000	-0.0010
				0.0000	-0.0010
				0.0000	-0.0010
			0.0020	0.0021	+0.0001
				0.0020	0.0000
				0.0019	-0.0001
0.0050	0.0000	-0.0050	0.0050	0.0050	0.0000
	0.0000	-0.0050		0.0050	0.0000
	0.0000	-0.0050		0.0047	-0.0003
0.0100	0.0091	-0.0009	0.0100	0.0100	0.0000
	0.0113	+0.0013		0.0109	+0.0009
	0.0100	0.0000		0.0092	-0.0008
0.0500	0.0486	-0.0014	0.0400	0.0400	0.0000
	0.0507	+0.0007		0.0404	+0.0004
	0.0500	0.0000			
0.1000	0.1000	0.0000			
	0.0993	-0.0007			
	0.1030	+0.0030			

With this reagent cooling assisted precipitation greatly and increased the sensitivity. When standard potassium solutions were carried through simultaneously with the unknowns a minimum of 0.010 mg. of potassium per ml. could be determined with precipitation at room temperature, whereas 0.002 mg. per ml. could be determined at 0° C. Moreover, precipitation was completed within 2 hours at the lower temperature. The composition of the precipitate was found to be best represented by the formula $\text{K}_{1.35}\text{Ag}_{1.65}\text{Co}(\text{NO}_2)_6$. Using standard nitrite solutions for the colorimetric comparison, and a potassium-nitrite factor based on the latter formula, the potassium content of the unknown was calculated. In this manner a minimum of 0.050 mg. of potassium per ml. could

be determined with precipitation at room temperature and 0.002 at 0° C. Although an alcoholic precipitation medium increases the sensitivity of the sodium cobaltinitrite reagent, neither alcohol nor acetone was found to exert a beneficial influence upon the sensitivity of the silver cobaltinitrite reagent.

Determination of Potassium in Water

Ammonium and chloride (3) are the only commonly occurring ions in water that interfere with the qualitative silver cobaltinitrite test. In view of the previous satisfactory results by this method, precipitation of the potassium without first concentrating appeared feasible when the potassium occurred in quantities greater than 0.002 mg. potassium per ml.—that is, 2 p. p. m. Less than 0.002 mg. per ml. necessitated concentrating in an acid solution. Acetic acid was satisfactory for this purpose and concentrations as great as 0.08 *N* did not interfere materially with the precipitation.

The effect of the excess silver ion upon the recovery of potassium was determined by using reagents containing 1 and 2 per cent of silver nitrate. For practical purposes the concentration of the excess silver ion in the precipitation medium was twice as great with the second silver nitrate solution as with the first because, in either case, only an extremely small amount of silver was removed by precipitation. When using the more concentrated solution, somewhat larger amounts of potassium were apparently recovered; this was believed to be due to a higher silver-potassium ratio in the precipitate. Preferably but a slight excess of silver ion should be present from the precipitation of the chloride and, what is more important, the same concentration of excess silver should occur in both standard and unknown.

In the analysis of naturally occurring waters, if the water sample is very soft, distilled water is satisfactory for the dilution of the potassium standards; while for accurate analysis of waters of greater hardness a synthetic water of the same hardness as the unknown should be used for this purpose. The previous work with the silver cobaltinitrite reagent indicated the accuracy which may be expected with very soft water samples.

TABLE III. POTASSIUM RECOVERY FROM HARD WATER

Present Mg./ml.	Potassium Found Mg./ml.	Difference Mg./ml.
0.0020	0.0021	+0.0001
	0.0020	0.0000
0.0060	0.0067	+0.0007
	0.0060	0.0000
	0.0055	-0.0005
	0.0061	+0.0001
0.0100	0.0100	0.0000
	0.0094	-0.0006
	0.0102	+0.0002
	0.0097	-0.0003
0.0200	0.0201	+0.0001
	0.0200	0.0000
	0.0190	-0.0010
0.0400	0.0400	0.0000
	0.0402	+0.0002
	0.0392	-0.0008

The applicability of the method to hard waters was demonstrated by the recovery of potassium from a synthetic water of extreme hardness. A potassium-free synthetic water was prepared which contained the maximum concentration of each substance ordinarily found in hard waters (4). The magnesium and calcium for this solution were weighed as the carbonates and then dissolved in an excess of acetic acid; the excess acid prevented hydrolysis and precipitation of iron, etc. This solution was 0.17 *N* in respect to acetic acid, but after the addition of potassium and removal of chloride the acidity of the final potassium standards had been reduced to 0.05 *N*.

For the determination of potassium from the synthetic water medium, 30 ml. of standard potassium solution were added to 10 ml. of 8.3 per cent silver nitrate solution and then enough synthetic water was added to make a final volume of 100 ml. After thoroughly mixing, the precipitate was removed from a portion of the solution by centrifuging. Remaining in the supernatant solution was 0.55 per cent silver nitrate and 0.6 per cent acetic acid. The potassium content of this solution was determined with the silver cobaltinitrite reagent. The standards possessed the same ionic concentrations as the unknowns and were accorded the same treatment. The results are shown in Table III.

The recovery of potassium from the hard water medium was remarkably good, considering the small quantity of potassium and the large quantity of other ions involved. Moreover, the analyses were made with greater rapidity and accuracy than could be expected with the normal evaporation procedure.

Summary

When a 10 per cent acetic acid medium is used in the Greiss method for the determination of nitrite, Beer's law is valid over a wide range. Since the intensity of the color is somewhat dependent upon the time interval between the addition of the sulfanilic acid and 1-naphthylamine, the accuracy of the method is improved by mixing the reagents before use.

The Tischer method for potassium is not applicable to the determination of less than 0.120 mg. per ml. of solution. Somewhat less than 0.080 mg. per ml. may be determined if comparison is made with potassium standards that have been given an identical treatment. By precipitating from a 30 volume-per cent alcoholic medium at 4° to 6° C., the minimum quantity of potassium determinable may be decreased to about 0.003 mg. per ml. of solution.

By employing a silver cobaltinitrite precipitating reagent, and running potassium standards simultaneously, the minimum quantity of potassium determinable is reduced to about 0.002 mg. Precipitation should be allowed to take place near 0° C., and an acetone wash liquor used. This method was found to be applicable to the determination of potassium in fresh water.

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The Design of a Precision Photoelectric Colorimeter

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AMONG the first applications of the modern photoelectric cell was its use to replace the human eye in photometric measurements. Many circuits and cell arrangements for specialized types of photoelectric photometry have been proposed in the literature (4, 8, 13, 17). The earlier photometers were of the direct-reading type and employed a single photoelectric cell. In 1919, Gibson (8) of the Bureau of Standards described the null method for photometric measurements, using it for the routine photometry of lamps. The null method with two photoelectric cells eliminates many of the inaccuracies entering through direct reading.

More recently the photoelectric cell has received attention as a means of minimizing the human element as a factor in colorimetry. Müller (11) in 1928 described a photoelectric colorimeter of the direct-reading type and discussed its application to automatic titration and pH control. Since that time a large number of papers have appeared describing colorimeters which employ various circuit arrangements and types of photoelectric cells (1, 10, 12, 14, 15, 16). While these papers have adequately discussed the detailed features of each colorimeter in question, there seems to be lacking in the literature a discussion of certain fundamental principles especially applicable to the general design of photoelectric colorimeters.

The design of a photoelectric colorimeter is determined largely by the inherent limitations of the photoelectric cell type employed and of the optical system. The following discussion will deal, first, with the manner in which these elements influence the characteristics of a precision photoelectric colorimeter and, second, with the general details of design of a precision instrument.

Photoelectric Cell Characteristics

RECTIFIER TYPE.¹ The rapid progress made in photoelectric colorimetry since 1932 has been due largely to the development of the rectifier type of photoelectric cell which is very rugged, sensitive, and capable of generating its own e. m. f. It requires no batteries or external source of electrical energy for satisfactory operation.

The complicated manner in which the internal resistance changes with light intensity, temperature, and time prevent the rectifier cell from being entirely suitable for the most precise colorimetric work. If the external circuit resistance is low (less than 100 ohms) in comparison to the internal cell resistance, so that the shunting effect of the latter is relatively small, the response becomes a linear function of light intensity to within 1 or 2 per cent.

The internal resistance also has a positive temperature coefficient for low external resistances and low intensities of radiation. Therefore precautions must be taken in the design of a colorimeter employing these cells to eliminate heating effects due to the light source. Further precaution should be made to allow sufficient time for each reading, since several minutes are required for the internal resistance to come to

¹ The rectifier type of cell consists essentially of a metal disk, upon one side of which is a surface of cuprous oxide or selenium, specially treated for maximum sensitivity to visible radiation. These cells have been referred to in the literature by such various terms as photogalvanic, photovoltaic, photoelectric, photonic, and rectifier.

complete equilibrium for each change in radiation intensity. The relatively low and variable internal resistance precludes the adaptability of these cells to vacuum tube amplification.

In Figure 1 is shown the spectral response curve of a typical rectifier cell. The sensitivity is high throughout most of the visible spectrum. The relatively low sensitivity in the red is of little consequence when the cell is used with incandescent lamps in which the peak of the spectral energy distribution curve occurs in the near infrared (900 millimu for projection lamps).

A circuit employing two rectifier cells in a bridge arrangement is presented in Figure 2. The arrangement is such that the external resistance for each cell under conditions of balance for the galvanometer, G , is always constant and equal and of a sufficiently low value that the response is essentially linear. R_1 and R_2 are a pair of dial decade resistances, so connected that if the system is balanced with the absorption cell out of the beam of light to P_1 , then the balance which is obtained with the absorption cell in the path of light to P_1 will be in direct proportion to the resistance included between the two contact arms. Thus such a dial decade may very readily be made to read in terms of percentage transmittancy of the absorbing medium. Such a colorimeter in simplified form has been satisfactorily used by the authors for work requiring accuracies of from 1 to 2 per cent. As discussed below this arrangement may be made to be fully compensating for fluctuations in the light source.

PHOTOEMISSION TYPE.² The characteristics of the photoemission type of photoelectric cell have been adequately described by Ives and Kingsbury (9) and others (2, 17). These cells in the vacuum type are almost exclusively used in laboratory precision photometry. Those commonly employed have either potassium hydride or cesium oxide cathodes. The gas cell is not generally suitable for accurate

² The term photoemission is applied to those cells which depend upon the emission of photoelectrons from a sensitized cathode, generally of an alkali metal surface of the halide, oxide, sulfide, etc., in an evacuated envelope (vacuum type) or in a rarefied atmosphere of inert gases (gas type).

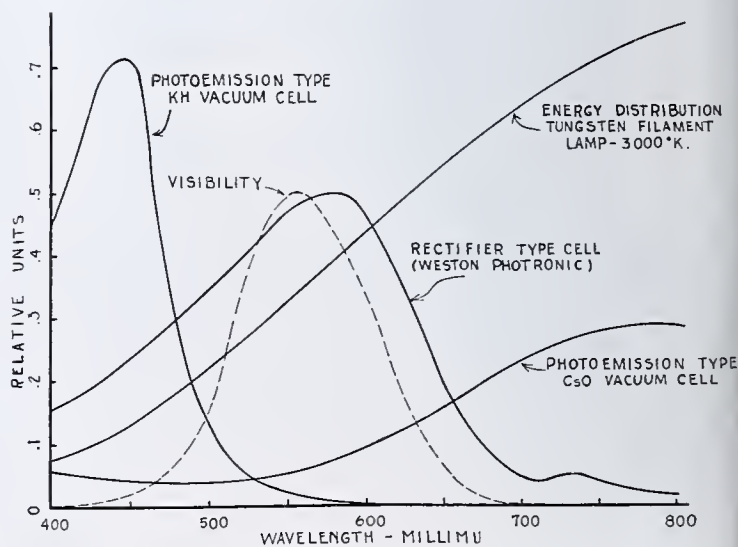


FIGURE 1. SPECTRAL RESPONSE CURVES OF PHOTOELECTRIC CELLS

quantitative work, owing to its relatively unstable current-voltage characteristic and the lack of a strictly linear relationship between light intensity and cell current.

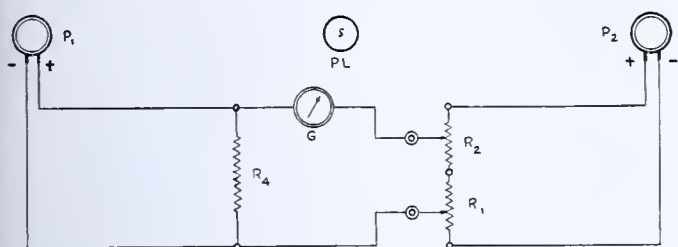


FIGURE 2. BRIDGE CIRCUIT FOR A PAIR OF RECTIFIER CELLS (PHOTONIC)

- R_1 . Dial decade 10×10 ohms, accuracy -0.1 per cent
 R_2 . Dial decade 10×1 ohms, accuracy -0.1 per cent
 R_3 . 100 ohms wire-wound fixed resistor

The modern vacuum cell has very stable electrical characteristics with a high internal resistance of the order of hundreds of megohms and a linear relationship of response to light intensity. The current sensitivity is low in comparison to that of the rectifier cell, but the high internal resistance makes these cells especially suited to vacuum tube amplification. By applying a saturating voltage to the vacuum cell it can be made relatively independent in response to small voltage fluctuations as may occur because of IR drop in the load resistance or line voltage. For a typical cesium oxide cell (Cetron) this saturation point is about 40 volts. An applied voltage above this point may vary 10 per cent without affecting the cell current by more than 1 per cent. In general, it may be stated that the load or external circuit resistance should not introduce an IR drop of more than one volt for accurate determinations based upon the cell retaining a linear response.

Ives and Kingsbury (9) present evidence to show that it is not safe to assume that the spectral sensitivity of an emission type of photoelectric cell is the same from month to month or like that of another cell, even though apparently manufactured under identical conditions. The relative instability of the spectral characteristics necessitates the use of narrow band pass light filters for precision colorimeters and nephelometers. The same considerations probably hold to the same degree in the case of the rectifier cell.

The spectral response curves in Figure 1 for the potassium hydride and the cesium oxide cells are those of Ives and show to the same scale the relative spectral sensitivity of these two types of cell. The other curves of Figure 1 are not drawn to the same scale. For general use throughout the visible spectrum and especially in the red, the cesium oxide cell is the better type. For the quantitative determination of yellow and red pigments having absorption maxima in the blue, the potassium hydride cell or a cell of similar spectral characteristics is better because of its high sensitivity in the blue and green (Westinghouse SR 51).

In Figure 8 is shown a bridge circuit for use with the vacuum photoemission cell. It operates on the same principle as that shown in Figure 2 for rectifier cells. With the vacuum emission cells, the load resistance need not be constant quantities, provided the total resistance is not high enough to produce an appreciable IR drop. It is possible to use three dial decade resistances in units of multiples of ten, making transmittancy readings possible to 0.1 per cent.

The saturating voltage consists of the alternating current voltage drop in R_6 and R_7 and for a 110-volt supply is 45 volts per cell. Since electrons can pass in appreciable numbers only from the cathode to the anode, the cells may be used to rectify the alternating current and a direct current galvanometer may be used. Only half of the alternating current wave

passes through the cell so that the theoretical current efficiency can be only 50 per cent of that of a direct current supply. Actually it is less, being about 45 per cent, owing to the fact that the voltage is too low for electron flow on the low portion of the wave. When the maximum cell sensitivity is required, the resistance R_6 and R_7 may be replaced with a pair of 45- to 90-volt radio B batteries.

Some Optical Systems Applicable to Photoelectric Colorimetry

The optical system of a balanced double photoelectric cell colorimeter may be considered as consisting of a lamp source mounted between and on the same optical axis with two identical optically independent portions, each terminating in a photoelectric cell. Each half of the system, in its most complete form, consists of (1) condensing lenses for concentrating as intense and homogeneous a beam of radiation as possible upon the photocell, and (2) radiation filters for spectrally limiting the radiation as emitted by the lamp source. In most cases condensing lenses are necessary to compensate for the great loss in total radiation occasioned by the use of narrow band pass filters. Without filters it is possible to mount the photocells close enough to the lamp to obtain sufficient radiation without the use of condensing lenses. However, proper filtering offers so many advantages in increased sensitivity, more linear calibration curves, greater stability, and more complete line voltage compensation that the unfiltered precision colorimeter is desirable only for certain specialized applications. In Figure 3 are shown several types of optical systems which may be employed. In diagrams A and B, the condensing lenses are of the small-diameter, short-focus type used in the small motion picture projectors. In diagram C is shown a method of using small precision absorption cells. The lamp source in this case must be small, such as a headlight bulb or strip filament projection lamp.

Systems of lenses often tend to produce an image of the source upon the photoelectric cell cathode, even though the cell may be considerably out of focus. This results in a series of bright bands when filament projection lamps are used. Ives and Kingsbury (9) have shown that the cathode of a photoemission cell may vary greatly in sensitivity over its surface. It is well known that these cells have an upper limit of intensity beyond which injury to the sensitive surface may

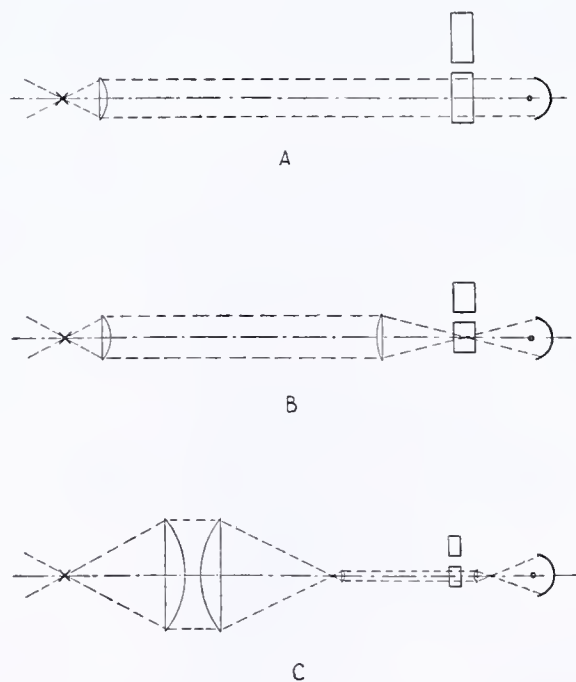


FIGURE 3. OPTICAL SYSTEMS FOR PHOTOELECTRIC COLORIMETERS

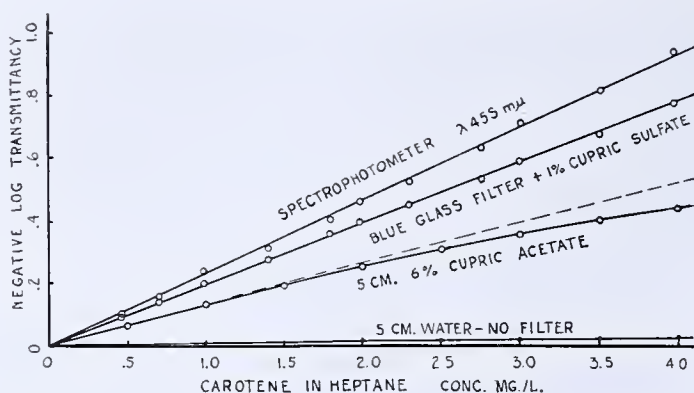


FIGURE 4. CALIBRATION CURVES FOR CAROTENE WITH VARIOUS DEGREES OF FILTERING

occur. For these reasons especially, the imaging effects are undesirable. In the case of the rectifier cell, the manner in which the shunting effect of the internal resistance changes with light intensity makes such effects equally undesirable. A diffusing screen of some of the finely molded diffusing window glasses, placed immediately in front of the photocell, adequately eliminates imaging effects without too serious a loss in radiation. In one test it was found that a piece of Diffusex glass scattered the light satisfactorily without incurring a loss of more than 25 per cent in cell response.

Properly spaced diaphragms are necessary to eliminate any scattered extraneous radiation that might reach the photoelectric cell. A diaphragm with an aperture slightly smaller than that of the absorption cell is necessary immediately in front of the absorption cell on the lamp side. Diaphragms having apertures of a wide range of diameters are valuable in limiting the total radiation reaching the photocell to an intensity which is noninjurious to the cell surface. Most small photoemission cells have a maximum safe emission of from 10 to 20 microamperes. The rectifier cell, on the other hand, is claimed by the manufacturers to be uninjured by high radiation intensities.

The radiant energy of the incandescent projection lamp is over 90 per cent infrared which is of no value in most colorimetric work. In order to produce high visible intensities without excessive heating of the absorbing media and photocells, it is necessary to remove the infrared by proper filtering. A water cell will absorb most of the energy beyond 1400 millimu. More complete filtering may be obtained by the addition of infrared absorbing glasses. The Corning 0.32-cm.

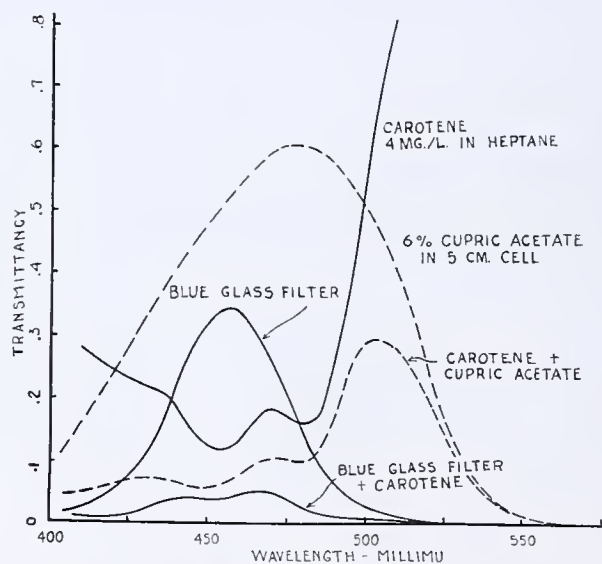


FIGURE 5. TRANSMISSION CURVES FOR CAROTENE AND VARIOUS FILTER COMBINATIONS

(0.125-inch) Aklo plate glass (3, 7) is very satisfactory for this purpose.

Assuming that sufficient radiant energy is available, the use of narrow band pass filters very greatly increases the sensitivity of a colorimeter. This increase in some cases may be as great as a hundred fold. The logarithmic calibration curves shown in Figure 4 are for carotene in heptane and graphically show the effect of various degrees of filtering. Carotene has absorption maxima only in the blue (Figure 5) so that unless filters are used, little effect on the total response of a cesium oxide photocell would be expected for large changes in carotene concentration. This is due to the masking effect of other radiation not selectively absorbed. When no filter is used, the curve has a very small slope and changes in the highest concentrations are barely detectable. With a 6 per cent cupric acetate filter (Figure 5) which has a relatively wide transmission band, the slope is greater than with no filter but not so great as in the case of a Jena glass filter combination of BG12 and GG5 (blue glass filter), the transmission band of which centers on the carotene absorption band. The steepest slope is obtained with a visual spectrophotometer in which the spectrometer functions as an optical filter transmitting a waveband of only a few millimu.

The filtering effect of an absorbing medium contained in the absorption cell may seriously alter the linear relationship of a logarithmic calibration curve, even though the absorbing medium itself obeys Beer's law. A comparison of the calibration curves for carotene obtained with two different filters used in a colorimeter employing a pair of cesium oxide cells shows this relationship (Figure 4). With the use of a 5-cm. cell of 6 per cent cupric acetate which has a wide transmission band, the calibration curve is not a straight line but falls off at the higher concentrations. At high concentrations, carotene has an appreciable filtering effect of its own and does not absorb equally over the transmission band of the filter. The resultant filtering effect of the carotene (4 mg. per liter) and the cupric acetate is shown in Figure 5. A decided maximum occurs in the longer wave lengths of the band. The presence of this off-peak maximum accounts for the deviation of the calibration curve from a linear relationship.

The case is different with the blue Jena glass filter in combination with the 1 per cent cupric sulfate solution. Here the filter band is so narrow that it is rather completely covered by the carotene absorption band. The transmission band resulting from a combination of the blue glass and carotene is reasonably symmetrical and has no off-peak maximum. The calibration curve is practically linear, as is also true in the case of the spectrophotometer.

Stable band pass light filters add greatly to the accuracy with which a double photoelectric cell colorimeter operating into a bridge circuit is compensated for variations in intensity of the light source due to line voltage fluctuations. Since slight voltage fluctuations are greatly magnified in terms of variations in light intensity, very complete compensation is necessary when a colorimeter is to be used on the average power supply. The only alternative to compensation in the instrument itself is voltage control by such devices as storage batteries and constant power transformers, which are bulky, expensive, and generally less satisfactory.

In the case of either of the bridge circuits shown in Figures 2 and 8, the same proportionate change in response of both cells will not affect the balance of the galvanometer if the potentiometer has been previously adjusted for zero deflection. If, however, the responses do not change in the same proportionate degree, the galvanometer will cease to be on zero deflection. As the temperature of the filament changes because of voltage fluctuations, the radiation emitted by the lamp will change, not only in intensity but in quality also.

The change in quality is due to the shift in spectral energy distribution of the filament with temperature. Therefore, the unfiltered radiation will produce equally proportionate changes in cell response only if the cells are identical in relative spectral sensitivity. This condition is very difficult to obtain even with present-day photoelectric cells. If the radiation from the lamp is filtered by a pair of identical narrow band pass filters, only a small but equal portion of the spectral sensitivity curve of each photocell is excited and difference in relative sensitivity on either side of the narrow spectral range transmitted by the filter is of no consequence. Under these conditions of filtering, it has been found that it is not necessary to have closely matched photoelectric cells for satisfactory line voltage compensation.

There are several types of light filters available for colorimetric work. The glass filters, such as the Corning (3) and Jena (6), are the most satisfactory from the standpoint of stability but they are often lacking in sharpness of transmission band. The cemented dyed gelatin filters, such as those made by Eastman (5), are more satisfactory as filters but in most cases lack the great stability of the glass types just mentioned. In general, it is best to select glass filters when possible and to use the less permanent dyed gelatin type only when sufficiently narrow transmission bands are not obtainable in the glass type.

Details of Colorimeter

The photoelectric colorimeter shown in Figure 9 and represented diagrammatically in Figures 7 and 8 was designed around a pair of Cetron (Continental Electric Company) cesium oxide vacuum photoelectric cells of the emission type (P_1 and P_2). The various parts of the instrument are mounted rigidly on a solid base of oak. Rigidity is a prime requisite for a satisfactory colorimeter of this type, since the slightest distortion of the base will deflect the light beam enough to cause annoying drifting of the galvanometer. An iron casting is excellent as a base.

The housing, H , is of 19-gage cadmium-plated black iron, and is divided into seven compartments by sheet-iron partitions. Adequate ventilation is provided in the lamp compartment by openings in the side and a short chimney on the top. A pair of readily removable aluminum lids exposes the two compartments at either end, which house the photocells and absorption cells. These are shown in the photograph.

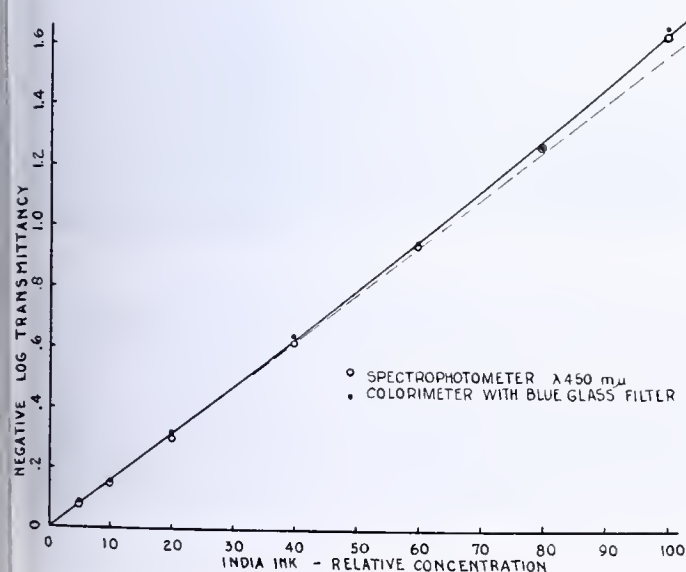


FIGURE 6. INDIA INK CALIBRATION CURVES

Obtained with a Bausch and Lomb spectrophotometer and the photoelectric colorimeter

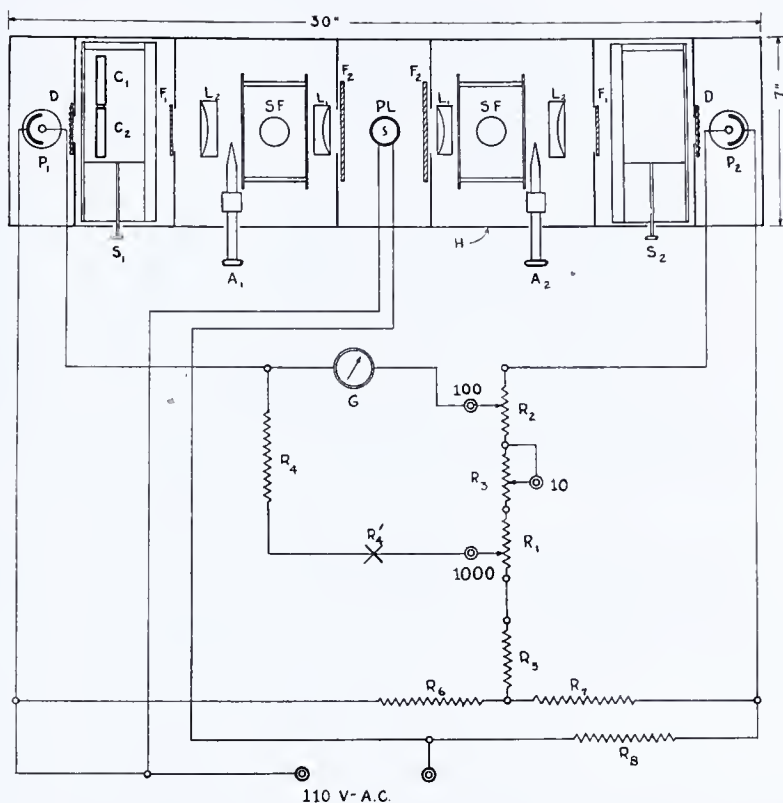


FIGURE 7. DIAGRAMMATIC VIEW OF COLORIMETER AND BRIDGE CIRCUIT EMPLOYED

- PL. 100-watt projection lamp, 2.1875-inch light center
- F_1 . $\frac{1}{8}$ -inch Aklo plate glass
- L_1 . Condensing lens, 5.625-cm. (2.25-inch) focus (Leitz 2.5 \times hand lens)
- SF. Solution filter cell, 5 cm. (Zeiss water cell)
- F_2 . Narrow band pass filter
- C_1, C_2 . Absorption cells
- D. Diffuse glass
- P_1, P_2 . Cesium oxide vacuum photoelectric cell (Continental Electric Co. "Cetron")
- S_1, S_2 . Absorption cell slide handle
- A_1, A_2 . Adjustment for balancing light flux
- H. Iron housing
- G. Galvanometer, short period type, sensitivity 0.0005 mm. 1 μ a.
- R_1 . Dial decade, 10×1000 ohms
- R_2 . Dial decade, 10×100 ohms
- R_3 . Dial decade, 10×10 ohms
- R_4 . 10,000-ohm wire-wound fixed resistor
- R_4' . 1000-ohm slide wire rheostat for balancing (optional)
- R_5, R_6, R_7 . 10,000-ohm wire-wound fixed resistor
- R_8 . 1000-ohm wire-wound fixed resistor

The lamp source, PL , is a 100-watt T-10 projection lamp in a medium pefocus base. The lamp has a light center of 5.47 cm. (2.1875 inches). The selection of lamps with this light center distance makes it possible to use 100-, 200-, and 500-watt lamps interchangeably in the same socket and still have the filament at the same focal point.

The lenses are Leitz hand magnifiers. L_1 is 50 mm. in diameter, 4 magnification, and L_2 is 54 mm. in diameter, 2.5 magnification. The lamp filament is at the focus of L_1 .

The filter system consists of a pair of panes of 0.3-cm. (0.125-inch) Aklo plate glass, F_2 ; a pair of Zeiss 5-cm. deep absorption cells, SF, for solution filters or water; and provision for inserting a pair of 5-cm. (2-inch) square glass or cemented gelatin filters, F_1 . The diffusing screen, D , is Diffuse glass.

The solutions of unknown density are placed in the absorption cell, C_1 , and the solvent is placed in cell C_2 . The two cells ride on a sliding carriage which moves by the handle, S_1 , between movable stops. In some types of determinations it is desirable to place absorption cells in both light paths and therefore a second carriage was incorporated at S_2 .

The tapered screws, A_1 and A_2 , are for finely balancing the radiant energy of the two beams. Since the radiation is essentially parallel between the two lenses, L_1 and L_2 , the addition of an opaque object does not result in seriously uneven flux distribution on the photoelectric cells.

The bridge circuit shown diagrammatically in Figure 7 and in detail in Figure 8 was made up as shown.

The dial decade resistances are accurate to 0.1 per cent. The fixed resistances, R_4, R_5, R_6, R_7 , and R_8 are wire-wound units having a tolerance of 1 per cent.

Attempts to use a slide wire rheostat type of potentiometer in place of the dial decade units have not proved very satisfactory. Such high-resistance potentiometers do not hold their calibration,

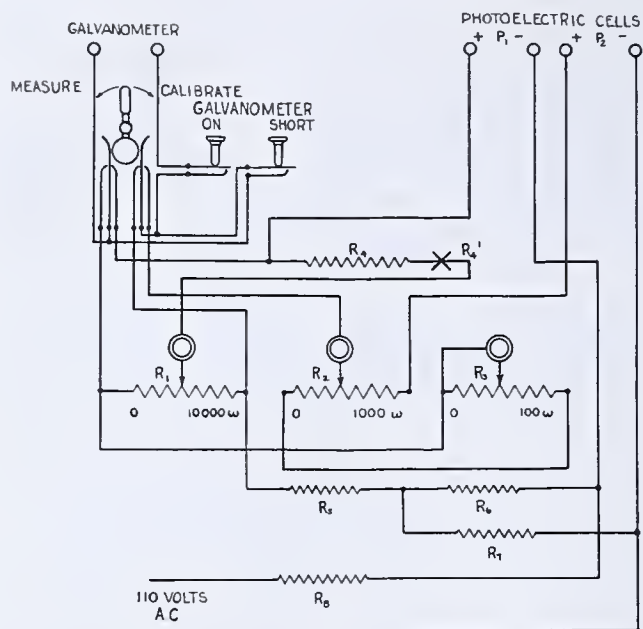


FIGURE 8. DETAILS OF A BRIDGE CIRCUIT FOR VACUUM PHOTOEMISSION CELLS
Elements are as described in Figure 7.

because of wear and movements of the wires under the sliding contact. Furthermore, most potentiometers of this type are not wound to an accuracy of better than 5 or 10 per cent.

The decade resistances are arranged on the instrument panel in the order shown in Figure 8, with the high unit on the left. The readings are made in terms of per cent in units of 0.1.

The double-pole, double-throw key switch is for quickly setting the bridge for calibration, with the decade units set for a total resistance of 10,000 ohms, regardless of the position of the decade switch arms. With this setting of the switch, the light intensity is balanced by means of the screws, A_1 and A_2 , with the blank absorption cell, C_2 , in place. The balancing can be made just as readily by means of a rheostat of 1000 or 2000 ohms at R_4' when vacuum emission cells are used.

After the instrument is balanced, the switch is thrown to "measure" and the absorption cell, C_1 , which contains the solution to be measured, is slid into place. A new balance is now made, using the three dials, and the transmittancy is read directly.

Several methods were used to determine whether the instrument and the photocells were strictly linear. The Cetron photoelectric cells were found to be as closely linear in response to intensity with the bridge circuit used as the methods employed could detect. The most conclusive test made was the determination of the transmittancy of a series of India ink solutions of arbitrary concentrations, the determinations being made by means of the colorimeter and a Bausch and Lomb polarizing spectrophotometer. The data are plotted in Figure 6. Both sets of data present curves which fall very closely to the same line. The deviation from a straight line is probably due to the ink itself, since both sets of data show the same deviation.

The ability of the colorimeter to retain its calibration accurately over a period of 6 months is exemplified in Table I. These figures are the results secured with different lamp bulbs and different photocells.

A dilute India ink solution and a 5-cm. (2-inch) square of Corning glass No. 555 were used as absorbing media. The filter consisted of the Jena blue combination BG12 and GG5. Only a few tenths difference in reading is occasioned by the use of two different pairs of photoelectric cells. These cells are obviously not matched, since they were purchased from the manufacturer almost a year apart. The deviation is only 0.5 per cent when projection lamps of two different voltages are employed. When the transmittancy of the glass was determined over a period of 6 months, the reading likewise varied only a matter of 0.1 per cent. In order to attain these accuracies, it is necessary to allow the lamp to heat up for 20 or 30 minutes

TABLE I. RESULTS WITH DIFFERENT LAMP BULBS AND PHOTOCELLS

Date	Lamp Watts	No. of Photocell in Socket	Absorbing Medium	T %
		P_1	P_2	
6-30-35	100	1	2	India ink 47.8
6-30-35	100	2	1	India ink 47.8
6-30-35	100	3	1	India ink 47.8
6-30-35	100	4	1	India ink 47.9
6-30-35	100	3	4	India ink 47.8
6-30-35	100	1	2	Corning No. 555 61.7
6-30-35	100	2	1	Corning No. 555 61.7
6-30-35	100	1	3	Corning No. 555 61.8
6-30-35	100	1	4	Corning No. 555 61.8
6-30-35	100	3	4	Corning No. 555 61.6
6-31-35	100	1	2	Corning No. 555 61.7
6-31-35	200	1	2	Corning No. 555 62.1
4-14-35	100	1	2	Corning No. 555 60.3
4-18-35	100	1	2	Corning No. 555 60.3
4-20-35	100	1	2	Corning No. 555 60.3
4-21-35	100	1	2	Corning No. 555 60.3
4-23-35	100	1	2	Corning No. 555 60.3
5-27-35	100	1	2	Corning No. 555 60.3
6-15-35	100	1	2	Corning No. 555 60.3
6-25-35	100	1	2	Corning No. 555 60.2
7-31-35	100	1	2	Corning No. 555 60.2
8- 3-35	100	1	2	Corning No. 555 60.3
9-20-35	100	1	2	Corning No. 555 60.3
10- 3-35	100	1	2	Corning No. 555 60.4
10-14-35	100	1	2	Corning No. 555 60.3
10-24-35	100	1	2	Corning No. 555 60.3

TABLE II. CALIBRATION DATA OF POTASSIUM DICHROMATE SOLUTIONS WITH PHOTOELECTRIC COLORIMETER

Concentration G./100 cc.	T_1 %	T_2 %	T_3 %	T_4 %
0.002	96.6	96.5	96.55	96.5
0.010	84.9	84.9	84.85	84.7
0.020	72.6	72.8	72.8	72.5
0.030	62.5	62.8	62.8	62.5
0.050	47.7	48.3	48.35	47.9
0.070	37.7	37.9	38.3	38.0
0.100	27.8	28.4	28.4	28.2

before taking any readings. For ordinary accuracies of the order of 1 per cent, no appreciable time needs to be allowed. If the instrument had been more rigidly mounted on a cast-iron base, these heating effects would probably not have been so pronounced.

Table II presents a set of readings taken with potassium dichromate solutions by three different individuals over a period of 8 hours. With the exception of one concentration, the readings do not have a maximum variation of more

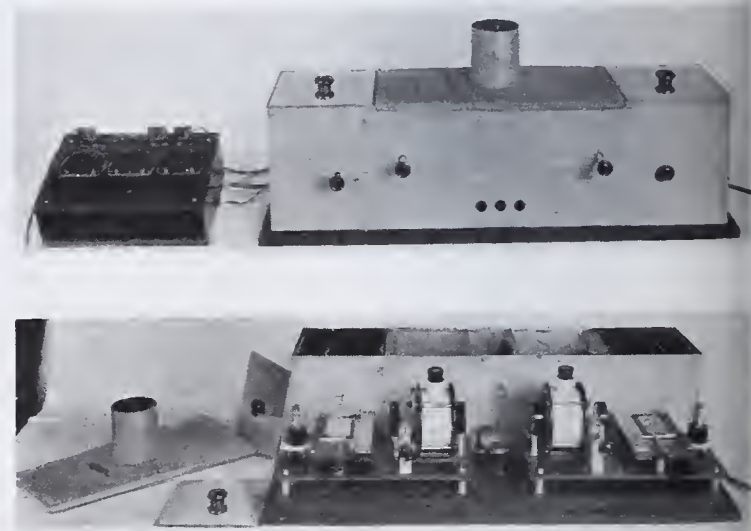


FIGURE 9. PHOTOGRAPH OF COMPLETED PHOTOELECTRIC COLORIMETER
Above, setup for use with bridge on left.
Below, colorimeter with housing removed to show placing of parts.

than 0.5 per cent. Some of this variation is undoubtedly due to foreign matter on the face of the absorption cells. It is very difficult to keep the cells absolutely clean when constantly refilling with solutions such as dichromate.

The degree to which the instrument is compensated for fluctuating line voltage was tested by inserting a variable resistance in series with the lamp source. The voltage was varied from 116 to 90 volts, which resulted in more than a 50 per cent decrease in light intensity. Under these conditions, the galvanometer balance did not shift sufficiently to necessitate a 0.1 per cent change in dial setting. This complete compensation is lost if the optical system is not filtered with absolute symmetry. For this reason, it is always advisable to purchase filters as matched pairs.

Summary

The principles of design of precision photoelectric colorimeters are discussed. An instrument based upon these principles is described which has the following characteristics:

The complete colorimeter consists of three units: colorimeter unit, dial decade bridge, and galvanometer, either wall or portable type depending upon the sensitivity required.

In measuring transmittancy, the instrument has an absolute accuracy of the order of 1 per cent and a reproducible accuracy of 0.1 per cent.

The accuracy of the instrument inherently depends only upon the retention of the linear response of the photoelectric cells and it is independent of other gradual changes in characteristics.

The calibration is not appreciably affected by changes in

lamp source or in line voltage fluctuations. Fluctuations of ± 5 volts are not detectable in the operation of the instrument. The colorimeter reads directly in percentage transmission. The instrument exhibits no lag effects.

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A Microdistillation Apparatus

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SUCCESSFUL chemical investigation of small amounts of material is largely dependent upon special manipulation designed to supply the same treatment as do the customary macroprocedures. Obviously microdistillation and fractionation require special technic because of the very small volume of the liquid. In the investigation of the ergot alkaloids which has been in progress in this laboratory for some time, it has been necessary to do many microdistillations. The apparatus described below was designed for this purpose and has proved invaluable to the work. Microsublimation followed by condensation on a small area has long been known. This apparatus, however, is an adaptation of the Siwoloboff (1) micromethod for taking boiling points, combined with an adaptation of the principle of microsublimation and allows a true distillation to be approached.

A diagram of the apparatus is shown in Figure 1. The main part of the apparatus is made from glass tubing approximately 17 mm. in diameter. The lower part is drawn out into a capillary which is about 30 mm. long and has an inside diameter slightly larger than 1 mm. On the lower end of the capillary is sealed a small, thin-walled bulb, A, of 0.25-cc. capacity. Projecting through and almost filling the capillary and extending to the bottom of the bulb is an ebullition stick, B, made of a solid glass rod, with the exception of the lower end on which is sealed 1 mm. of capillary tubing. The condenser, C, is fitted into the apparatus with a ground-glass joint at F. Its top is closed by a rubber stopper through which a glass tube, D, extends to the lower end of the condenser. The condenser is cooled by a stream of cold water entering through the glass tube, D, filling the condenser, and emerging at G. During the distillation, liquid condenses on

the outside of the tip of C and is held there by surface attraction. In order that more liquid may adhere to the tip of the condenser, it is strongly indented. By making the proper inverted cup on the tip, 0.2 cc. of a mobile organic liquid will easily adhere. Following distillation, the distillate can be removed from the condenser by means of a capillary pipet and the tip of the condenser then placed in a small, short test tube and the last traces of distillate removed with the appropriate solvent.

The apparatus is immersed in an oil bath to a point above the tip of the condenser as shown. The oil bath is fitted with a mechanical stirrer and a thermometer for recording the temperature. The temperature of the oil bath is slowly raised until the liquid visibly boils or until a steady stream of

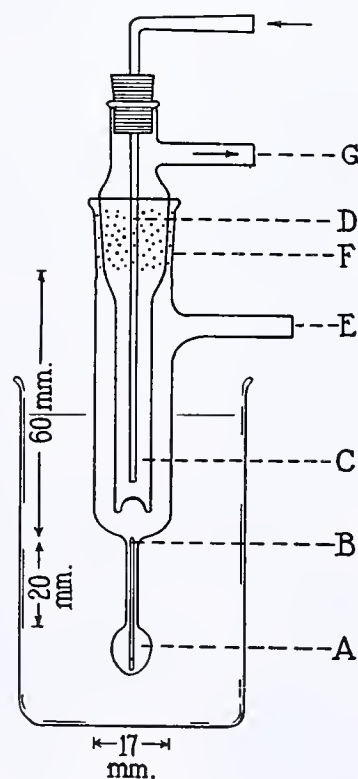


FIGURE 1

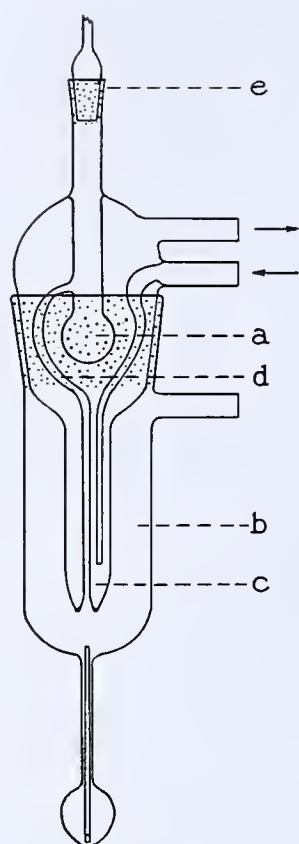


FIGURE 2

essentially only at the boiling point of the liquid. Herein lies the advantage of the apparatus described, since, without the capillary, vapors would pass from the liquid to the condenser at a temperature considerably below the boiling point because of evaporation and rapid diffusion to the condenser through the larger opening. The conditions presented by distillation

bubbles comes from the tip of the ebullition stick, *B*. In order to determine the boiling point, experience has shown that a correction of a few degrees must be subtracted from the temperature of the oil bath at this point. The boiling point is of the same order of accuracy as the boiling point taken by the Siwoloboff micromethod (1) for taking boiling points. An indication of the boiling point can be obtained only when the liquid is a pure compound, since the temperature recorded gives the boiling point of the liquid and not that of the distillate. When fractionation is necessary, each fraction is redistilled and the true boiling point thus approached.

The liquid to be distilled is placed in the bulb, *A*, by means of a capillary pipet and the ebullition stick, *B*, is then replaced. *B* fits the capillary of the apparatus rather snugly and allows passage of the vapors of the liquid to the condenser, *C*,

from the customary flasks used for macrodistillation are thus more nearly reached by use of the capillary constriction which is nearly filled by the ebullition stick, *B*.

As many fractions as desired can be taken during each distillation. Each fraction, however, corresponds to only a flash distillation, as there is no fractionation from reflux. A complete distillation can be done very quickly and is practically quantitative, as only the condenser is below the temperature of the boiling point of the liquid and there is no loss due to a large condenser surface. Accordingly, the process may be repeated several times and thus arrive at a fractionation in the truest sense of the word. Distillations under reduced pressure can be made equally well by evacuating the flask at the opening, *E*, although one of the usual means of avoiding fluctuations of the pressure is necessary since the distillation must take place without bumping. Thus, the apparatus is adaptable for distillation of a wide range of substances at temperatures and pressures at which any distillation can be accomplished on the customary macroscale.

When the volume of the distillate is more than 0.2 cc., an apparatus of the type shown in Figure 2 has been found to be useful. This operates in principle like the previous apparatus, with the exception that provision has been made for the collection of the larger volume of distillate by modification of the condenser.

A capillary tube is fitted to the top of the condenser at *e* with a small ground-glass joint and leads to a mercury leveling bulb, the purpose of which is to change the pressure in the collection chamber, *a*, so that it can be made less than that in *b*. By proper adjustment, the droplet of distillate as it collects at *c* will be forced up through the capillary, *d*, and into *a*, where it can be obtained with a capillary pipet after the distillation is finished.

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Borax as an Acidimetric Standard

FRANK H. HURLEY, JR., Department of Chemistry, Rice Institute, Houston, Texas

THE use of borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, as a primary standard in acidimetry was suggested many years ago (8). Experimental work tending to confirm its suitability for this purpose has appeared from time to time (1, 4, 6), but it has never been as generally used as its many advantages would seem to warrant. Kolthoff (1), in comparing the relative merits of several substances as acidimetric standards, states that "the substance most to be recommended as a standard is borax." Lindfors (3) recommends it highly for routine commercial work. The most probable reason for the failure of borax to come into common use is that it is a hydrated compound, and such compounds are not usually suitable for use as standards because of the difficulty of drying them under conditions such that none of the water of hydration is lost.

The methods which have hitherto been proposed for drying borax are not entirely satisfactory. The process of simple air-drying of recrystallized borax recommended by Lindfors (3) is not very safe, because the solution which remains on the surface of the crystals is alkaline enough to absorb carbon dioxide from the air with the formation of sodium carbonate or bicarbonate as an impurity (2). The technic of drying borax over moist sodium bromide, which is recommended by Kolthoff (2), is open to two practical objections—namely,

that sodium bromide is relatively expensive, and that the drying process requires considerable time. Moreover, the suitability of this desiccant has recently been questioned by Menzel (5) on theoretical grounds. Menzel proposes in place of sodium bromide a solution saturated with respect to both sugar and salt (sucrose and sodium chloride), since this solution was found to have the proper vapor pressure for maintaining borax in the decahydrated state over a wide range of temperature. This last desiccant, while it is apparently free from all theoretical criticism, is nevertheless objectionable because of its slow action. Unless an easy, rapid, and exact method for drying borax is available, its usefulness as a standard substance is obviously limited. In the present paper, a very easy method of drying with alcohol and ether is described and the purity of borax dried in this way is tested by comparison with borax dried by Menzel's method and also with pure sodium carbonate.

Purification and Drying of Borax

Pure borax was prepared by the recrystallization of the c. p. material, using quantities of borax and water (50 m. of water to every 15 grams of borax) such that no crystallization could occur above 55°C ., thus eliminating the poss

bility of the formation of the pentahydrate of sodium tetraborate (transition temperature, decahydrate \rightleftharpoons pentahydrate, $61^{\circ}\text{C}.$). The borax crystals were freed from mother liquor by suction, then washed twice with water.

The first method of drying consisted in washing the damp crystals with two portions of 95 per cent ethyl alcohol, followed by two portions of ethyl ether, each washing being followed by suction to remove the wash liquid. The portions of alcohol and ether used were about 5 ml. for 10 grams of the borax crystals. This drying treatment has been applied with success in analytical work to magnesium ammonium phosphate hexahydrate. Following the treatment with alcohol and ether, the borax was spread out in a thin layer on a watch glass and allowed to stand at room temperature to permit the evaporation of the ether.

The second method of drying consisted in spreading the damp crystals on a watch glass and placing it in a desiccator over a solution saturated with respect to both sugar and salt, the desiccant recommended by Menzel.

Stability of Borax

Before proceeding to analytical tests of the purity of borax prepared and dried by the methods described, it was desired to gain some information about the stability of the substance in air at room temperature, and in the presence of saturated sugar and salt solution. One of the principal advantages in the use of borax is that it may be weighed directly in air, since it is not hygroscopic. It has long been known, however, that borax loses its water of crystallization very slowly when kept in air at room temperature. In order to determine the rate at which this loss occurs, a 3-gram sample of borax, dried with alcohol and ether and allowed to stand overnight to permit the evaporation of the ether, was placed in a crucible and allowed to remain for a long period of time in contact with air at room temperature (24° to $33^{\circ}\text{C}.$). From time to time the crucible was weighed and the loss in weight noted. The loss of weight at the end of several periods of exposure was as follows: 5 days, 0.027 per cent; 17 days, 0.050 per cent; 25 days, 0.076 per cent; 52 days, 1.04 per cent. During the first 25 days the loss in weight was regularly about 0.1 mg. per day. Between the fifty-second and fifty-third days the loss amounted to 1.6 mg. It appears, therefore, that the rate of loss of water, though very small at first, increases with time. It seems probable from these results that leaving borax for as long as a week or 10 days would be safe in ordinary work, except under very unusual conditions of temperature and humidity.

The stability of borax in the presence of saturated salt and sugar solution was also tested. Menzel (5) found that the maximum variation in weight of a sample of borax kept for 2 months in a vacuum desiccator over this solution amounted to only -0.02 per cent. To test the efficacy of this solution in the drying of borax, 3.5 grams of damp borax crystals were spread out on a watch glass and placed in a desiccator over this solution. After 3 days the crystals appeared to be quite dry. The loss in weight on the fourth day amounted to only 0.1 mg., and after 52 days to 0.9 mg. (0.026 per cent). Another 3.5-gram sample of borax which had been dried with alcohol and ether also showed a loss of 0.026 per cent in weight on standing over sugar-salt solution for 55 days. It appears from these measurements that the desiccant proposed by Menzel is satisfactory, and that borax may be safely stored over sugar-salt solution for an indefinite length of time.

A further study of the stability of borax is now in progress.

Purity of Borax Dried with Alcohol and Ether

To ascertain whether the alcohol-ether method of drying yields pure decahydrated borax, samples purified and dried by this method were compared with another sample dried by Menzel's method and also with pure sodium carbonate,

by means of hydrochloric acid. The borax dried with alcohol and ether was allowed to stand overnight before it was used. That dried over saturated sugar and salt was allowed to remain in the desiccator for a week. The pure sodium carbonate used for the comparison was prepared from c. p. sodium bicarbonate by the method of Reinitzer (?), and was dried to constant weight by heating at 270° to $300^{\circ}\text{C}.$

Standard solutions (0.05 M) of the borax samples and of sodium carbonate were prepared and 25-ml. portions of the solutions titrated with approximately 0.1 M hydrochloric acid. All the instruments used in the preparation of the standard solutions and in the titrations were calibrated to give an accuracy of 0.1 per cent or better.

In the borax titrations methyl red was used as the indicator, and the end point was matched with a color standard prepared by adding 5 drops of methyl red to 70 ml. of a solution containing 1.0 gram of sodium chloride and 2.2 grams of boric acid in 500 ml. of water. This solution represents approximately the stoichiometrical point of the titration of 25 ml. of 0.05 M borax with 0.1 M hydrochloric acid, assuming 20 ml. of wash water to be used in the titration. This color standard must be boiled to remove carbon dioxide which may be dissolved in the water. If properly prepared it has a straw color, different from the pure yellow of methyl red in alkaline solution, but not yet pink. By the use of the color standard the borax titration may be performed without titration error (2), for the stoichiometrical point of the titration comes within the range of color change of methyl red. However, the use of a color standard in routine work with borax is practically superfluous, since the color change of methyl red occurs so rapidly and is so distinct that the first change from pure yellow may be taken as the end point without making any serious error.

The sodium carbonate titrations were performed at the boiling point, using methyl red. Under these conditions the titration error amounts to less than 0.01 ml. of 0.1 M acid, which is beyond the limit of error of the buret readings. Methyl red was chosen in preference to methyl orange for the carbonate titration because the indistinctness of the methyl orange end point renders the measurements uncertain.

The molarity of the 0.1 M hydrochloric acid was calculated from titrations against three samples of borax, two of which were dried with alcohol and ether and one over sugar-salt solution, and from one sample of sodium carbonate. All four titrations gave the same molarity for the acid (0.1024 M). This concordance indicates that the alcohol-ether method of drying borax is entirely satisfactory. In view of the ease with which the method may be carried out, the only disadvantage which has hitherto prevented the extensive use of borax—namely, the difficulty of obtaining the dry salt—appears to be now obviated.

Acknowledgment

The writer wishes to thank Arthur F. Scott for his interest and coöperation in this work.

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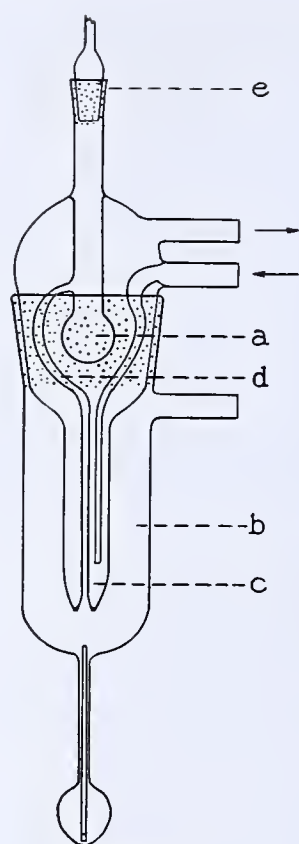


FIGURE 2

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The second method of drying consisted in spreading the damp crystals on a watch glass and placing it in a desiccator over a solution saturated with respect to both sugar and salt, the desiccant recommended by Menzel.

Stability of Borax

Before proceeding to analytical tests of the purity of borax prepared and dried by the methods described, it was desired to gain some information about the stability of the substance in air at room temperature, and in the presence of saturated sugar and salt solution. One of the principal advantages in the use of borax is that it may be weighed directly in air, since it is not hygroscopic. It has long been known, however, that borax loses its water of crystallization very slowly when kept in air at room temperature. In order to determine the rate at which this loss occurs, a 3-gram sample of borax, dried with alcohol and ether and allowed to stand overnight to permit the evaporation of the ether, was placed in a crucible and allowed to remain for a long period of time in contact with air at room temperature (24° to 33° C.). From time to time the crucible was weighed and the loss in weight noted. The loss of weight at the end of several periods of exposure was as follows: 5 days, 0.027 per cent; 17 days, 0.050 per cent; 25 days, 0.076 per cent; 52 days, 1.04 per cent. During the first 25 days the loss in weight was regularly about 0.1 mg. per day. Between the fifty-second and fifty-third days the loss amounted to 1.6 mg. It appears, therefore, that the rate of loss of water, though very small at first, increases with time. It seems probable from these results that leaving borax for as long as a week or 10 days would be safe in ordinary work, except under very unusual conditions of temperature and humidity.

The stability of borax in the presence of saturated salt and sugar solution was also tested. Menzel (5) found that the maximum variation in weight of a sample of borax kept for 12 months in a vacuum desiccator over this solution amounted to only -0.02 per cent. To test the efficacy of this solution in the drying of borax, 3.5 grams of damp borax crystals were spread out on a watch glass and placed in a desiccator over this solution. After 3 days the crystals appeared to be quite dry. The loss in weight on the fourth day amounted to only 0.1 mg., and after 52 days to 0.9 mg. (0.026 per cent). Another 3.5-gram sample of borax which had been dried with alcohol and ether also showed a loss of 0.026 per cent in weight on standing over sugar-salt solution for 55 days. It appears from these measurements that the desiccant proposed by Menzel is satisfactory, and that borax may be safely stored over sugar-salt solution for an indefinite length of time.

A further study of the stability of borax is now in progress.

Purity of Borax Dried with Alcohol and Ether

To ascertain whether the alcohol-ether method of drying yields pure decahydrated borax, samples purified and dried by this method were compared with another sample dried by Menzel's method and also with pure sodium carbonate,

by means of hydrochloric acid. The borax dried with alcohol and ether was allowed to stand overnight before it was used. That dried over saturated sugar and salt was allowed to remain in the desiccator for a week. The pure sodium carbonate used for the comparison was prepared from c. p. sodium bicarbonate by the method of Reinitzer (7), and was dried to constant weight by heating at 270° to 300° C.

Standard solutions (0.05 *M*) of the borax samples and of sodium carbonate were prepared and 25-ml. portions of the solutions titrated with approximately 0.1 *M* hydrochloric acid. All the instruments used in the preparation of the standard solutions and in the titrations were calibrated to give an accuracy of 0.1 per cent or better.

In the borax titrations methyl red was used as the indicator, and the end point was matched with a color standard prepared by adding 5 drops of methyl red to 70 ml. of a solution containing 1.0 gram of sodium chloride and 2.2 grams of boric acid in 500 ml. of water. This solution represents approximately the stoichiometrical point of the titration of 25 ml. of 0.05 *M* borax with 0.1 *M* hydrochloric acid, assuming 20 ml. of wash water to be used in the titration. This color standard must be boiled to remove carbon dioxide which may be dissolved in the water. If properly prepared it has a straw color, different from the pure yellow of methyl red in alkaline solution, but not yet pink. By the use of the color standard the borax titration may be performed without titration error (2), for the stoichiometrical point of the titration comes within the range of color change of methyl red. However, the use of a color standard in routine work with borax is practically superfluous, since the color change of methyl red occurs so rapidly and is so distinct that the first change from pure yellow may be taken as the end point without making any serious error.

The sodium carbonate titrations were performed at the boiling point, using methyl red. Under these conditions the titration error amounts to less than 0.01 ml. of 0.1 *M* acid, which is beyond the limit of error of the buret readings. Methyl red was chosen in preference to methyl orange for the carbonate titration because the indistinctness of the methyl orange end point renders the measurements uncertain.

The molarity of the 0.1 *M* hydrochloric acid was calculated from titrations against three samples of borax, two of which were dried with alcohol and ether and one over sugar-salt solution, and from one sample of sodium carbonate. All four titrations gave the same molarity for the acid (0.1024 *M*). This concordance indicates that the alcohol-ether method of drying borax is entirely satisfactory. In view of the ease with which the method may be carried out, the only disadvantage which has hitherto prevented the extensive use of borax—namely, the difficulty of obtaining the dry salt—appears to be now obviated.

Acknowledgment

The writer wishes to thank Arthur F. Scott for his interest and coöperation in this work.

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Loss of Pyrethrins during Analysis of Mineral Oil-Pyrethrum Extracts by the Seil Method

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MINERAL oil-pyrethrum sprays for household use are ordinarily perfumed to cover the objectionable mineral oil odor. The perfumes used usually contain esters or other compounds which interfere with the determination of the active principles, pyrethrin I and pyrethrin II, by methods based on the titration of their mono- and dicarboxylic acids. Seil (2) and Ripert (1) suggest steam distillation of such products to remove the perfume before proceeding with the analysis. Preliminary tests having indicated that there was a loss of pyrethrins in the analysis of these commercial extracts following Seil's procedure, a more complete study of the method was made.

Three preparations of the mineral oil-soluble portions of pyrethrum were prepared by extracting 750-gram portions of powdered pyrethrum in a large extractor with petroleum ether (boiling range 35° to 40° C.); the petroleum ether was evaporated by immersing the flask in a water bath, the temperature of which was maintained between 50° and 55° C., and the residue was then treated successively with 200-cc. portions of the oil solvent, filtered, and made to 6 liters with mineral oil. In the preparation of sample A a commercial purified white mineral oil of the type used as a base for commercial household fly sprays was used as a vehicle, and for samples B and C kerosene highly purified in the laboratory was used. (The purified kerosene used had a distillation range from 165° to 300° C. with 84 per cent distilling between 175° and 250°, while the fly spray oil base had a distillation range from 200° to 250° C.) No perfume or other interfering substances were added. These prepared samples were stored in brown glass bottles in a dark cupboard from which they were removed only during the actual time of sampling.

These preparations were analyzed by the Seil method, subjecting them to steam distillation just as though perfume were present. Since the volume of distillate necessary to remove all the perfume from commercial samples varies within rather wide limits, four 100-cc. aliquots of each sample were distilled and distillates of 250, 500, 1000, and 1500 cc., respectively, were collected, in order to simulate conditions met in the analysis of commercial samples. Pyrethrins were determined in the distillate as well as in the residue remaining in the distillation flask. As a means of comparison pyrethrins were also determined in the original samples without steam distillation.

In making the analyses the procedure outlined by Seil was followed as closely as possible. However, because of the for-

mation of emulsions during the steam distillation and also during the boiling off of the alcohol after the saponification, it was necessary to introduce slight modifications. The emulsion formed in the flask during the steam distillation was broken by adding a small quantity of saturated sodium sulfate solution and 25 to 50 cc. of petroleum ether. The emulsion formed during the boiling of the alkaline solution after saponification was more difficult to break, but separation usually was possible after adding a little petroleum ether and a few cubic centimeters of a 20 per cent sodium hydroxide solution.

After titrating for pyrethrin I in the portions of the distilled oil, the qualitative color test described by Seil (2) was also applied. In each case the test was positive, showing that the chrysanthemum monocarboxylic acid was definitely present.

The analytical results are given in Tables I and II. The results in Table I show that there is a progressive loss in the pyrethrin content of the sample during the steam distillation.

TABLE II. PYRETHRINS DETERMINED IN PYRETHRUM EXTRACTS WITHOUT STEAM DISTILLATION

Sample	Pyrethrin I Mg./100 cc.	Pyrethrin II Mg./100 cc.	Total Mg./100 cc.
A	31.7	45.2	76.9
B	36.4	47.5	83.9
C	24.6	52.0	76.6

In two cases the method of distillation was modified with the idea of holding a larger proportion of oil in the distillation flask. In the first case 100 cc. of the fly spray oil base were added to the aliquot to be distilled and in the second case 50 cc. of a highly purified mineral oil having a distillation range of from 300° to 400° C. were added before distillation. In each case there was a slight increase in the pyrethrins recovered but the loss was still considerable. This loss is only partially due to volatilization of the pyrethrins with the steam. A large part is due to decomposition or other chemical change, as is shown by the fact that the sum of the pyrethrins determined in the distillate and in the residue is considerably below the value obtained by direct saponification of the sample.

Summary

A study of the Seil method for the determination of pyrethrins in mineral oil extracts of pyrethrum shows that there is a loss of pyrethrins during the steam distillation for the removal of perfume. The loss is due to volatilization with steam and to decomposition or other chemical change. In the case of the materials here reported the loss approximated 25 per cent of the pyrethrins.

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TABLE I. PYRETHRINS DETERMINED IN PYRETHRUM EXTRACTS AFTER STEAM DISTILLATION

Sample	Volume of Distillate		Pyrethrins in Distillate			Pyrethrins in Residue			Total Mg./100 cc.
	Water	Oil	Pyreth- rin I	Pyreth- rin II	Total	Pyreth- rin I	Pyreth- rin II	Total	
	Cc.	Cc.	Mg./ 100 cc.	Mg./ 100 cc.	Mg./ 100 cc.	Mg./ 100 cc.	Mg./ 100 cc.	Mg./ 100 cc.	
A	250	...	4.1	3.4	7.5	24.0	34.6	58.6	66.1
	500	...	6.4	3.6	10.0	24.0	31.3	55.3	65.3
	1000	90	5.0	4.9	9.9	22.4	33.1	55.5	65.4
	1500	95	6.4	3.3	9.7	19.5	29.4	48.9	58.6
	500 ^a	105	Not determined			25.6	33.3	58.9	..
B	250	50	3.5	2.4	5.9	27.6	37.9	65.5	71.4
	500	75	4.3	3.2	7.5	26.7	35.4	62.1	69.6
	1000	80	4.3	2.2	6.5	25.4	31.5	56.9	63.4
	1500	90	4.3	2.6	6.9	23.7	32.2	55.9	62.8
	1000 ^b	70	3.3	2.0	5.3	26.9	34.0	60.9	66.2
C	250	50	5.6	2.0	7.6	12.6	34.0	46.6	54.2
	500	70	5.8	2.2	8.0	10.5	35.7	46.2	54.2
	1000	90	7.3	3.1	10.4	10.9	33.0	43.9	54.3
	1500	95	6.6	2.9	9.5	9.9	30.8	40.7	50.2

^a Distillation made after addition of 100 cc. of a commercial fly spray oil base.

^b Distillation made after addition of 50 cc. of purified high boiling mineral oil.

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A One-Piece Glass Micro-Kjeldahl Distillation Apparatus

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DESPITE the popularity and increasing use of the micro-Kjeldahl method for nitrogen determination, there have been few fundamental improvements of the distillation apparatus originated by Parnas and Wagner (3). Their design has a number of inherent drawbacks which are generally recognized. Schulek and Vastagh (4) criticize the use of rubber connections. In some cases these have been replaced by glass joints, but this increased the fragility of the apparatus and rendered it difficult to assemble. Neither did it improve the design with regard to the number of pieces to be mounted and table space occupied. Hoppe-Seyler (1) has eliminated a portion of the clumsiness of the apparatus, but has also increased fragility without a large gain in compactness.

Since it has been found in this laboratory and elsewhere (2) that condensers of Pyrex brand glass gave results identical to those of silver, a completely new Kjeldahl distillation apparatus was designed. (It was constructed through the cooperation of C. M. Flanders, Box 232, Berkeley, Calif., who can now supply this apparatus in quantity.)

Tests of this apparatus showed it to have a number of points of superiority over the usual type of equipment. All rubber connections were eliminated from the distillation train; danger of breakage was reduced by the strong, compact construction; multiple outfits were easily built up, because of the upright shape and small size; considerably less attention during the course of distillation was necessary; only one burner was used to operate the apparatus and one clamp to hold it in place; very little condensation of steam occurred in the flask; and no diminution in volume took place during distillation.

With a single distillation outfit, the time required for an analysis was not shortened; but, owing to the very slight attention required during distillation, one operator could conveniently operate a small battery and save time in this way. Only one precaution was found necessary, i. e., prevention of sucking back of the sample. This was readily accomplished by the procedure described below.

Experimental

The apparatus, shown in Figure 1, consists of a distillation flask, the bulb of which contains 25 to 35 ml., enclosed in a glass jacket which serves as a steam generator. A tube sealed inside the flask and opening into the generator leads steam through the solution being distilled. The arm of a Y in this tube is sealed through the wall above the generator to the filling funnel. Above

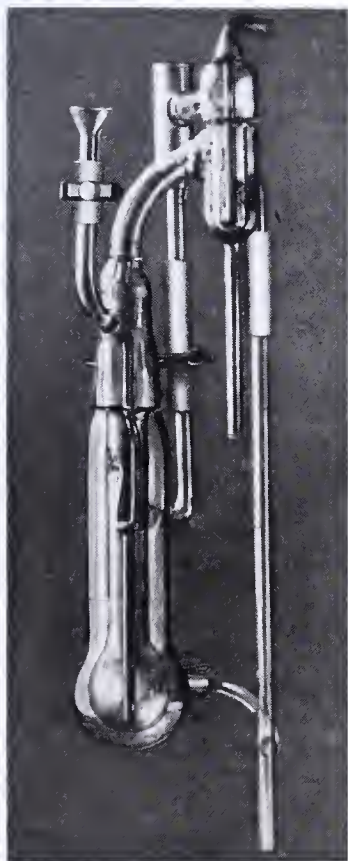


FIGURE 1

the flask is a trap and head leading to a small glass internal condenser which drains through a vertical delivery tube into the receiver. An overflow and by-pass carry the condenser water either to the drain or to the steam generator, which is equipped with an auxiliary drain tube. The total height of the apparatus is 35 cm. (14 inches). The steam generator jacket is 42 mm. in diameter and 16 cm. in height, the bulb being 60 mm. in diameter. The internal effective portion of the condenser is 18 mm. in diameter and 55 mm. in length.

TABLE I. ANALYSIS OF NITROGEN-CONTAINING SOLUTIONS

Substance	Sample Nitrogen Mg.	Nitrogen Found Mg.	Error %
(NH ₄) ₂ SO ₄	0.210	0.2096	-0.2
		0.2082	-0.8
		0.2082	-0.8
		0.2096	-0.2
(NH ₄) ₂ SO ₄	0.418	0.420	+0.5
		0.417	-0.2
		0.420	+0.5
		0.420	+0.5
Urea	0.792	0.783	-1.1
		0.787	-0.6
		0.786	-0.7
		0.785	-0.8
<i>p</i> -Amino benzoic acid	0.388	0.387	-0.3
		0.388	0000
		0.387	-0.3
		0.388	0000
<i>p</i> -Amino benzoic acid	0.762	0.758	-0.5
		0.761	-0.1
		0.762	0000

Around the steam generator may be wrapped an insulating asbestos jacket (not shown) to prevent sudden cooling from draughts. A few boiling chips of porcelain or silicon carbide are used in the generator to prevent irregular boiling. Silicon carbide chips are superior to those of porcelain. It was found desirable to use a moderate flame for the initial heating and a strong flame as soon as boiling started. Only at this point was there any tendency to suck back. As soon as distillation started, no further attention was necessary.

The apparatus was used in a fashion similar to the usual micro-Kjeldahl distillation. The digested sample was rinsed in through the filling funnel, followed by the caustic, with formation of two layers in the flask. With the by-pass and generator drains closed with pinchcocks, the water in the generator was heated to boiling and the steam distillation continued for 5 minutes, after which the receiver was lowered and rinsed internally by heating 1 or 2 minutes longer. The outside of the delivery tube was rinsed into the receiver. On removing the flame, the condensation of steam served to suck the contents of the flask into the generator. This usually required about a minute, and could be accomplished instantaneously by opening the by-pass pinchcock momentarily, thus admitting a trickle of cold water. The flask was rinsed with distilled water which promptly sucked into the generator. The generator drain was opened, followed by the by-pass, thus allowing the condenser water to flush out the generator, an operation requiring only a short time. The apparatus was then ready for the next sample, which could be introduced while the generator was still being flushed.

Some typical analyses are shown in Table I. Excellent

checks were readily obtained, though the absolute accuracy of the method is not notably different from the usual micro-Kjeldahl, since no fundamental operations are altered. Modifications tending to eliminate inherent errors may be made as easily as with the older forms of equipment.

This work was aided by a grant from the Research Board of the University of California.

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Laboratory Bubble-Cap Columns of Glass

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This paper contains a description of two all-glass bubble-cap columns of a greatly improved design. These columns are exceedingly easy to operate and may be used for vapor velocities up to 31.3 and 65.5 cm. (1.0 and 2.2 feet) per second, respectively. Since the height of the equivalent theoretical plate of one of these columns is about 2 cm., it is now feasible to build columns with separating powers equivalent to between 100 and 150 theoretical plates in a laboratory of average height.

IN PREVIOUS papers (2, 3) various all-glass bubble-cap columns for laboratory use have been described. These columns have been used extensively for many years by a variety of different laboratories and have been found exceptionally valuable, particularly for distillations of mixtures containing organic compounds that tend to undergo decomposition or chemical changes under the catalytic influence of metal packings.

Since the time of the last publication it has become apparent to the writer that important improvements in the efficiency of these columns could be made if the height of the

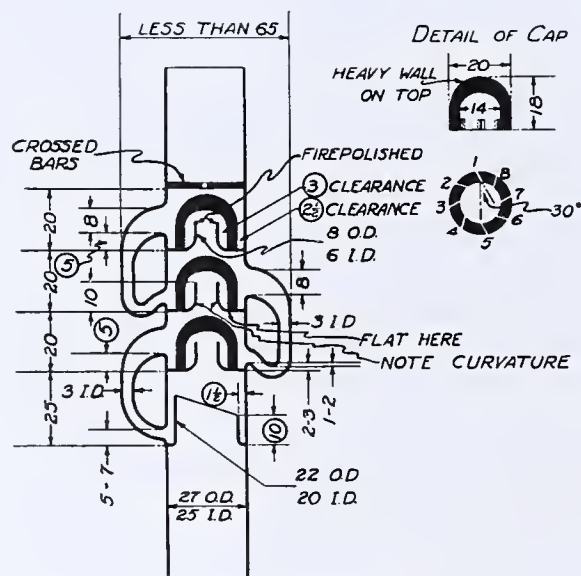


FIGURE 1. REDESIGNED BUBBLE-CAP COLUMN, 2-CM. SECTIONS

Slots in bubble cap, as shown, about 0.5 to 1 mm. wide and 3 mm. deep, at an angle of 30° with radius, fire-polished. Material, Pyrex laboratory glass. All dimensions are in millimeters. Exact dimensions are circled.

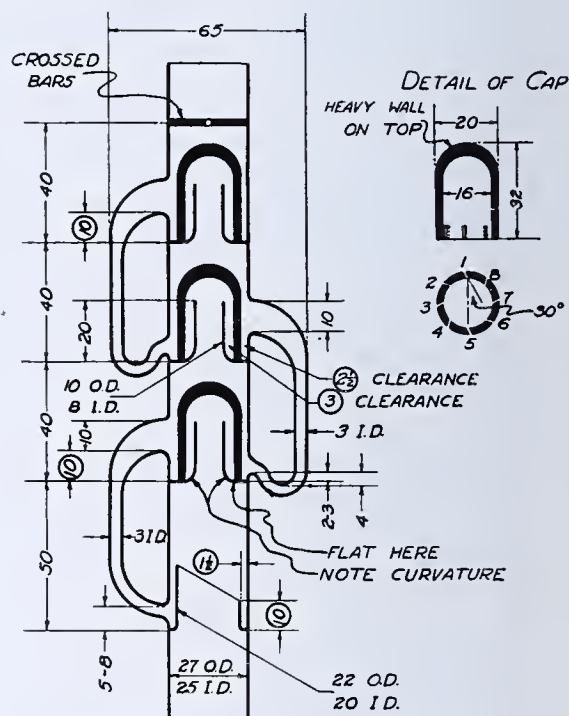


FIGURE 2. REDESIGNED BUBBLE-CAP COLUMN, 4-CM. SECTIONS

Slots in bubble cap, as shown, about 0.5 to 1 mm. wide and 5 mm. deep, at an angle of 30° with radius, fire-polished. Material, Pyrex laboratory glass. All dimensions are in millimeters. Exact dimensions are circled.

individual plate sections could be reduced without a corresponding sacrifice in vapor velocity.

Reconstruction of the Bubble-Cap Column

A series of short (2-plate) experimental columns having the same internal diameter, but of different designs and dimensions, was made up successively, and tested with respect to vapor velocity, holdup, plate efficiency, ease of operation, etc. The data obtained during the operation of these experimental columns have led to a complete redesign of the glass bubble-cap column, with the result that the degree of separation (number of theoretical plates per meter) now obtainable by columns of the new design is up to 400 per cent as high as that obtained with the old column of the same height and diameter.

Detail drawings of the redesigned bubble-cap columns are given in Figures 1 and 2. While these figures represent columns containing only three plates each in addition to the liquid seal customarily used between the still pot and the column, any desired number of plates may be added to the columns. Readers who are not familiar with the working principles of these columns are referred to the earlier paper (3).

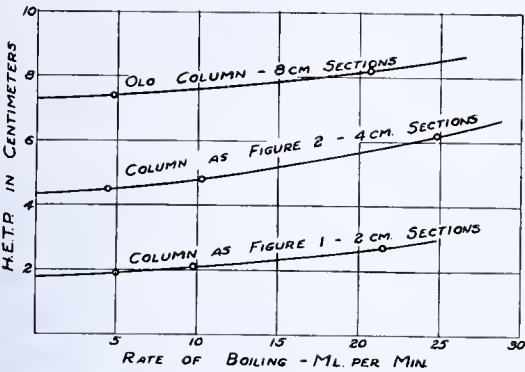


FIGURE 3. VARIATIONS OF THE HEIGHT OF THE EQUIVALENT THEORETICAL PLATE WITH RATE OF BOILING

Carbon tetrachloride-benzene mixture

By comparing the columns shown in Figures 1 and 2 with that of the same internal diameter described in the earlier publication (3), it may be noted that the following major improvements have been made:

- 1. The "holdup" of liquid per section has been reduced to a mere fraction of its former value. Thus the columns shown in Figures 1 and 2 have holdups of 0.7 and 1.4 ml., respectively, per plate, which represent only about 16 and 32 per cent, respectively, of the former holdup (4.4 ml.). These values apply to the columns while in normal operation, during which about 50 to 60 per cent of the liquid on the plate is displaced by vapor.
- 2. The vertical slots in the bubble caps have been ground at an angle of about 30° with the radii, in such a manner that the vapor bubbles will be forced to describe a circular motion around the bubble caps. This will naturally lead, not only to a more intimate contact and prolonged rectification between the ascending vapor and the descending reflux liquid, but also to a decided improvement in the circulation of the liquid on the plates. It is also believed that the new type of slots will have a tendency to reduce entrainment at higher rates of distillation.

TABLE I. EFFICIENCY RUNS USING MIXTURES OF CARBON TETRACHLORIDE AND BENZENE (TOTAL REFLUX)						
Column (25-Mm. Inside Diameter)	Height of Column Cm.	Rate of Boiling Ml./min.	Mole per cent of CCl ₄		Number of Theoretical Plates - 1	H.E.-T.P. Cm.
5-Plate column in 2-cm. sections (Figure 1)	10	5.1	26.6	44.6	5.4	1.9
		9.8	26.6	42.9	4.8	2.1
		21.5	26.6	39.7	3.7	2.7
5-Plate column in 4-cm. sections (Figure 2)	20	4.5	27.1	42.4	4.4	4.5
		10.3	27.1	41.6	4.2	4.8
		24.6	26.9	39.7	3.7	5.4
5-Plate column in 8-cm. sections, old column (3)	40	4.8	26.6	45.6	5.7	7.1
		20.7	26.6	43.1	4.9	8.2

TABLE II. EFFICIENCY TEST RUNS USING MIXTURES OF n-HEPTANE AND TOLUENE (TOTAL REFLUX)						
Column (25-Mm. Inside Diameter)	Height of Column Cm.	Rate of Boiling Ml./min.	Mole per cent of C ₇ H ₁₆		Number of Theoretical Plates - 1	H.E.-T.P. Cm.
5-Plate column in 2-cm. sections (Figure 1)	10	2.5	9.9	57	4.9	2.0
		5.1	9.9	55.2	4.7	2.1
		10	9.9	52.5	4.3	2.3
		20	9.9	48.7	3.8	2.6
5-Plate column in 4-cm. sections (Figure 2)	20	3.6	9.9	58	5.1	3.9
		7.5	9.9	55	4.7	4.3
		11.7	9.9	53.2	4.4	4.5
		20.7	9.9	51.0	4.2	4.8
		31.2	9.9	49.8	4.0	5.0
5-Plate column in 8-cm. sections, old column (3)	40	7.3	9.9	57.5	5.0	8.0
		22.0	9.9	57.5	5.0	8.0
		29.3	9.9	54.5	4.6	8.7

3. Perhaps the most important improvement is the elimination of the excessive vapor friction exhibited by the earlier bubble-cap columns through an unproportionally high liquid head in the side arms. This vapor friction constituted a serious drawback, inasmuch as the individual plate sections had to be made unnecessarily high (8 cm.) if the columns were to be used for ordinary rates of distillation. The cause of the friction was found to be inadequate clearance between the "vapor riser" and the bubble cap. By providing a clearance of 2.5 to 3 mm. at this point, the author has found that, at ordinary rates of boiling, the liquid level in the side arms rarely rises above the value corresponding to the hydrostatic head of the plate above (Figure 5).

4. The hydrostatic pressure difference between two successive plates—that is, the height of the liquid on each plate—has been reduced from 30 mm. in the older column to 5 mm. in the column described in Figure 1 and to 10 mm. in the column shown in Figure 2. Because of the more intimate contact provided between the vapor and liquid by the above-mentioned angular slots, this reduction has been accomplished without an appreciable sacrifice in plate efficiency.

As shown in Figures 1 and 2, the height of each plate section, formerly 80 mm., has been decreased to 20 and 40 mm., respectively. This accomplishment obviously reduces the height of a column containing a certain desired number of actual plates to one-fourth and one-half, respectively, of its former value.

Efficiency Data on the New Column

In order to obtain strictly comparable data on the relative efficiencies of the reconstructed and the older type bubble-cap columns, a 5-plate column was made of each of the three types and tested under identical and carefully controlled conditions. Each column was surrounded by means of an electrically heated transite jacket, provided with glass windows and thermometers, so that the columns could be operated without heat loss during the test runs. For each efficiency run a charge of 1500 ml. of the test mixture was used, and the column was allowed to operate under total reflux until equilibrium had been obtained. The rate of boiling at the top of the column was calculated by the usual method (4) from the amount of heat absorbed by the condenser water. A sample was taken from the top of the column as well as from the still pot, and from the analysis (by means of refractive index) of these fractions and from the vapor-liquid composition diagrams, the theoretical number of plates required to effect the accomplished separation was calculated by the method of McCabe and Thiele (5). By dividing the actual height of the column used by the number of theoretical plates corresponding to the degree of separation effected, the height of the equivalent theoretical plate (H.E.T.P.) was derived. Account was taken of the separation accomplished in the still pot by subtracting one plate from the theoretical number deduced from the McCabe-Thiele diagram. The results of the efficiency runs are tabulated in Tables I and II.

Each of the three columns was carefully tested at various rates of boiling and by means of two different kinds of test

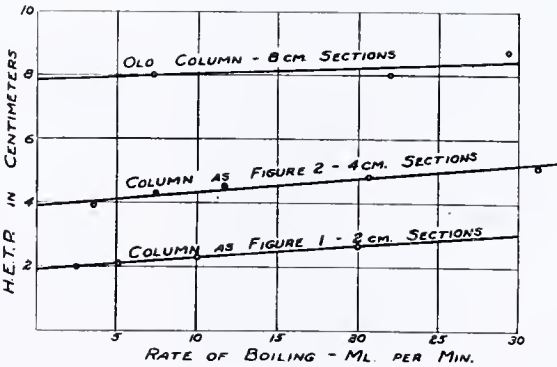


FIGURE 4. VARIATIONS OF THE HEIGHT OF THE EQUIVALENT THEORETICAL PLATE WITH RATE OF BOILING

n-Heptane-toluene mixture

mixtures, notably, carbon tetrachloride-benzene (difference in boiling points = 4.1° C.) and *n*-heptane-toluene (difference in boiling points = 12° C.).

The vapor-liquid composition diagram as well as the refractive index curve for the carbon tetrachloride-benzene system was calculated from the data published by Rosanoff and Easley (6), while the corresponding data for the system heptane-toluene were taken from the experimental values (based upon density measurements) of Bromiley and Quiggle (1).

In Tables I and II, it is noted that while the heights of the three columns used are widely different and vary from 10 up to 40 cm., the effected separations of the test mixtures are very much the same. As a result of the reconstruction of the bubble-cap column the height of the equivalent theoretical plate has been reduced from about 8 cm., in the case of the older column, to about 2 cm. for the column shown in Figure 1.

For the lower rates of boiling, some of the plate efficiencies obtained were above 100 per cent. It is believed that this inconsistency was contributed largely by errors in data used for the construction of the vapor-liquid composition curve, since a comparatively small error in this diagram will have a large effect upon the calculated plate efficiency.

In Figures 3 and 4, the heights of the equivalent theoretical plates for the various columns have been plotted against the rate of boiling. The effect of the rate of boiling is small in comparison with the difference in height of the equivalent theoretical plate between the various columns tested. Thus the column shown in Figure 1, for instance, even if operated at a rate of 21.5 ml. per minute, or near its maximum or most inefficient rate, would still have an "H. E. T. P." which would only be about 38 per cent of that of the old column operated at its minimum or optimum rate (see Figure 3).

TABLE III. MAXIMUM VAPOR VELOCITIES AND RATES OF BOILING

Column	Rate of Boiling at Top of Column, Ml./Min. of Benzene	Vapor Velocity at Top of Column	
		Cm./sec.	Ft./sec.
As shown in Figure 1, 20-mm. sections	30	31.3	1.0
As shown in Figure 2, 40-mm. sections	64	65.5	2.2
Old design (3), 80-mm. sections	41	42.4	1.4

Table III shows the maximum vapor velocities and rates of boiling at which the columns, in the absence of bumping, may be operated without flooding. Since these tests were carried out with benzene, it is evident that a higher rate of boiling in milliliters per minute should be expected if liquids of higher molecular weights were used.

Conclusions

Referring to the column shown in Figure 1, it is noted that the height of the equivalent theoretical plate for this column is only about 2 cm. (about 0.75 inch). This value appears to be smaller than that reported for any other column in the literature, regardless of the diameter.

The column shown in Figure 2 can be used for vapor velocities up to 65.5 cm. per second (2.2 feet per second) as against 31.3 cm. per second (1.0 feet per second) for the column shown in Figure 1, and is therefore recommended for use in laboratories where speed of distillation is essential. For most purposes, however, the column shown in Figure 1 is to be preferred, since the degree of separation in this column is 200 per cent as great as that obtained in the column shown in Figure 2 and about 400 per cent as great as the older type of bubble-cap columns.

In a laboratory of average height, it is possible to build a column containing between 100 and 150 plates (height 2 and 3 meters, respectively) of the design shown in Figure 1, while only half that number of plates could be used with the column shown in Figure 2.

While it has been shown that the efficiency as well as the throughput of columns containing metal packings decreases as a result of corrosion (4), the columns described in this paper have the obvious advantage of retaining their efficiencies indefinitely. Thus, strictly reproducible results can be obtained over indefinite periods of time.

As the older type of all-glass bubble-cap columns has been shipped by the manufacturer to distant places, and as they have been used extensively by many laboratories without a single reported breakage, it is believed that the new columns, properly mounted (3), should be at least as sturdy and long-lasting.

The new columns are exceedingly easy to operate. For a given liquid the jacket temperatures may be varied within wide limits without causing any disturbances or flooding, and the columns require, practically speaking, no attention except that of charging as well as removal of the distillate fractions. Another unique feature of the new columns is the fact that it is possible for the operator, by a glance at the liquid levels in the side arms, to get a rough indication of the rate of boiling. As shown in Figure 5, the liquid level is considerably higher up in the arm when the column is operating near its flooding point. With this in mind, the column may be adjusted to a safe operating rate and then left, more or less, to take care of itself.

Manufacturing of Columns

The columns described in this paper have been made by the Otto R. Greiner Company, 55 Plane St., Newark, N. J. In order to avoid any misunderstanding, it should be noted that both of the columns described in this paper (Figures 1 and 2) are entirely different and much superior to an unpublished column (40-mm. sections) which has been designed by the author and made by the same manufacturer during the past two years.

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RECEIVED February 10, 1936. Presented before the Division of Petroleum Chemistry at the 91st Meeting of the American Chemical Society, Kansas City, Mo., April 13 to 17, 1936.

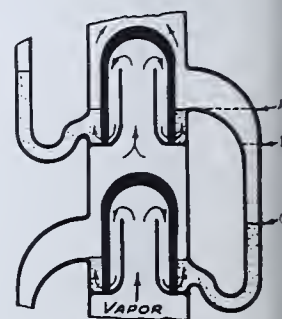


FIGURE 5. OPERATING RATE OF COLUMN AS A FUNCTION OF LIQUID LEVEL IN SIDE ARMS

- A. Flooding point
B. Maximum operating rate
C. Normal operating rate



A Simple Laboratory Shaking Machine

JOHN H. HIGHBERGER, Department of Leather Research, University of Cincinnati, Cincinnati, Ohio

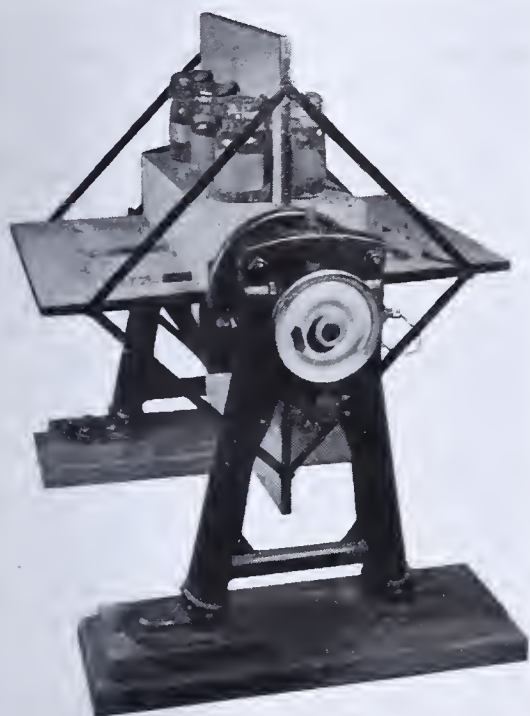


FIGURE 1. LARGE MODEL

MOST of the laboratory shaking machines on the market suffer from the faults of overcomplication and lack of adaptability. Inasmuch as agitation is a frequent and important operation in this laboratory, both in analytical and experimental work, considerable thought was devoted to the design of a machine which would present the utmost in simplicity and versatility. It was particularly desired to keep as simple as possible the method of holding in place the containers to be agitated, and at the same time permit the simultaneous use of different sizes of vessels on the machine. The principle adopted to these ends, and incorporated in the two machines shown in Figures 1 and 2, has been in satisfactory use in this laboratory for the past 3 years.

The larger of the two machines, shown in Figure 1, will accommodate 24 bottles of any size up to about 2 liters. The body consists of a rectangular box 30.5 × 30.5 × 61 cm. (12 × 12 × 24 inches), from each side of which projects a 30.5 × 61 cm. (12 × 4 inch) board, mounted on its long edge along the center line of the box. The boards, which are of 1.91-cm. (0.75-inch) stock, are fastened to the box with screws, and held rigidly in place by means of 1.91-cm. (0.75-inch) strap iron supports. Three slots, 5.1 × 17.8 cm. (2 × 7 inches), are cut in the lower side of each board, next to the face of the box. The whole is mounted, by means of two short lengths of 3.014-cm. (1.187-inch) steel shaft secured to the ends of the box by means of metal face plates, between two inverted pressed-steel shaft hangers, which serve as supports. Ring oiling bearings are used in the hangers, which are 58.4-cm. (23-inch) drop, mounted on wooden blocks so that the shaft center is 67.3 cm. (26.5 inches) above the floor. The machine is rotated by a belt drive through a speed reducer of 50 to 1 ratio, driven by a 0.25 h. p. motor. Speeds of 30 to 60 r. p. m. are satisfactory for most purposes, and may easily be altered to suit the particular work by means of multiple pulleys.

The essential idea of the machine is the method of holding the containers in place. For this purpose use is made of large regular elastics cut from discarded rubber inner tubes. For most sizes of bottles or jars these are most satisfactorily cut

in 6.4- to 7.6-cm. (2.5- to 3-inch) widths. Such an elastic is slipped around the container, which is then set on the box next to one of the slots. The elastic is then pulled through the slot from the other side of the board, and stretched to permit the insertion of a second container on that side. The containers are thus securely held in pairs, one on each side of the board, and their attaching or removal is merely a matter of slipping the elastic on or off. For the larger sizes of containers the elastics should be cut from one of the large-size inner tubes used in truck tires. These are easily obtainable at most garages.

For use with smaller sizes of containers the modification shown in Figure 2 was suggested by W. P. Doelger of this department. The same method of fastening the bottles on the machine is used, but as the weight is not so great in this case, no base is necessary for them to rest on, and they are supported only by the elastics passed through the slots as before.

The apparatus consists essentially of a 2.54-cm. (1-inch) oak board, 91.4 cm. (36 inches) long, which rotates about its long axis. Five 5.1 × 20.3 cm. (2 × 8 inch) slots make it possible to accommodate 10 containers. The board is suspended between two shaft hangers by means of two 20.3-cm. (8-inch) lengths of 2.54-cm. (1-inch) steel shaft, each of which is welded to a pipe flange bolted to one of the end pieces of the board. The shaft hangers are of 20.3-cm. (8-inch) drop and are mounted by means of wooden blocks so that the shaft center is 24.1 cm. (9.5 inches) above the table top. The machine is driven by a 0.125 h. p. motor operating through a speed reducer of 50 to 1 ratio.



FIGURE 2. SMALL MODEL

The relative cheapness of such a machine is realized from the fact that the cost of the smaller model was approximately fifty dollars. This includes the motor and speed reducer, and the cost of welding the pipe flanges to the shaft. The cost of the larger model is naturally somewhat higher, principally because of the use of larger shaft hangers and motor. A saving could probably be effected in the construction of these machines by the substitution of wooden supports for the pressed-steel shaft hangers, but the convenience and neat appearance of the latter, together with the ease with which the shaft may be properly aligned by means of their adjusting screws, makes their added expense well justified.

Acknowledgment

The writer is indebted to E. K. Moore of this department for much help in the design and construction of these machines.

RECEIVED March 12, 1936.

Nomographs for Determining Molecular Weights by the Freezing Point and Boiling Point Methods

W. S. GILFOIL, Omega, La.

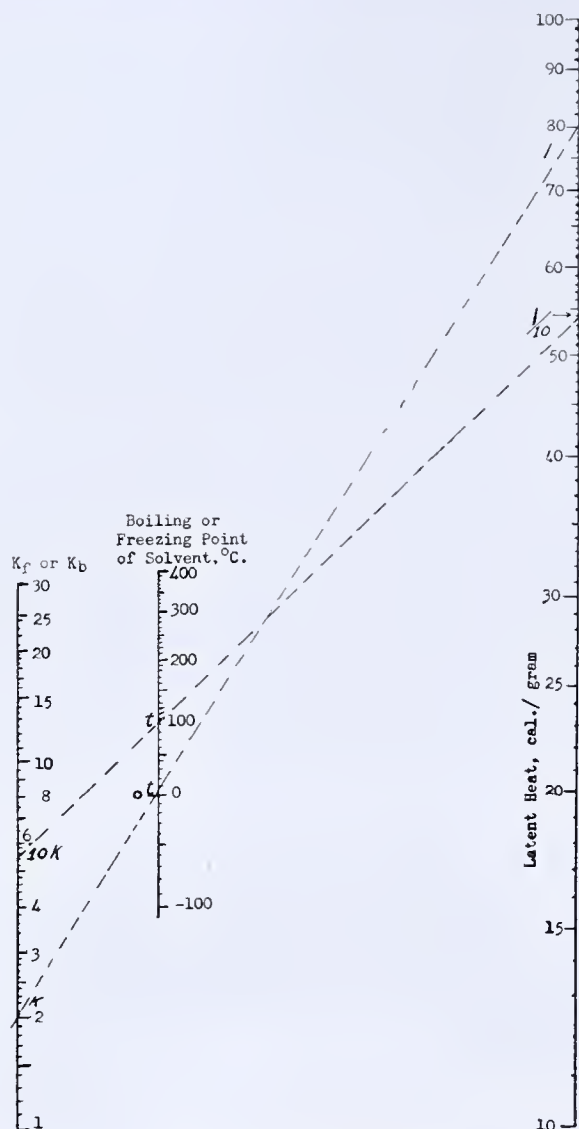


FIGURE 1. NOMOGRAPH

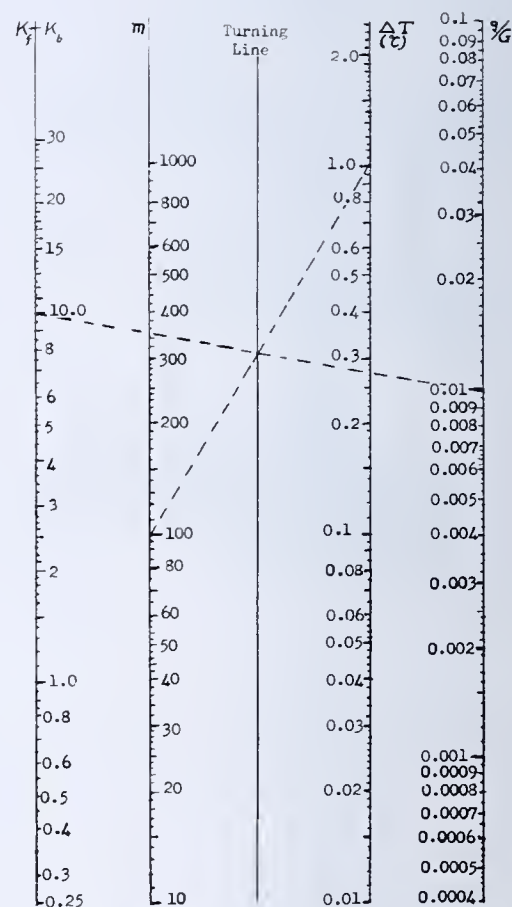


FIGURE 2. MOLECULAR WEIGHT NOMOGRAPH

$$m = 1000 \frac{K \times g/G}{\Delta T}$$

THE determination of molecular weights is a common step after the ultimate organic analysis of a compound. As a rule the data obtained are less accurate than the nomographs, which are satisfactory for all practical purposes. The method makes use of two sets of analogous equations. The boiling point equations are the same as those given here for the freezing point method, and the same charts are used for both.

$$K_f = T_0^2 / 503 l_f \quad (1)$$

$$m = 1000 K_f \times g / G \times \Delta T_f \quad (2)$$

where K_f represents the molal depression of the freezing point
 T_0 , the freezing point of the solvent in degrees Kelvin
 l_f , the latent heat of fusion in calories per gram
 g , the weight of solvent
 G , the weight of solute, expressed in the same units
 m , the molecular weight of the solute
 ΔT_f , the observed freezing point depression

In case a value falls off the chart, as in the case of l_f for water, divide by 10 (for simplicity's sake); running the line from 53.9 through 100°C. , we obtain a value on the K_f line which, when divided by the same number, 10, gives the proper value of K_f (Figure 1).

In the formation of the second nomograph (Figure 2), as there are four variables, a turning line is necessary. Its use may be illustrated by the following example:

Experimental data give a ratio g/G of 0.010, the difference in temperature between the freezing point of solvent and solution was 1.000°C. , and K_f was 10.0. Draw a straight line from 10 on the K line to 0.01 on the g/G line. From the point where this line intersects the turning line, draw a straight line through the m line and the point 1.000 on the ΔT line. The value of m is then read as 100, the proper value.

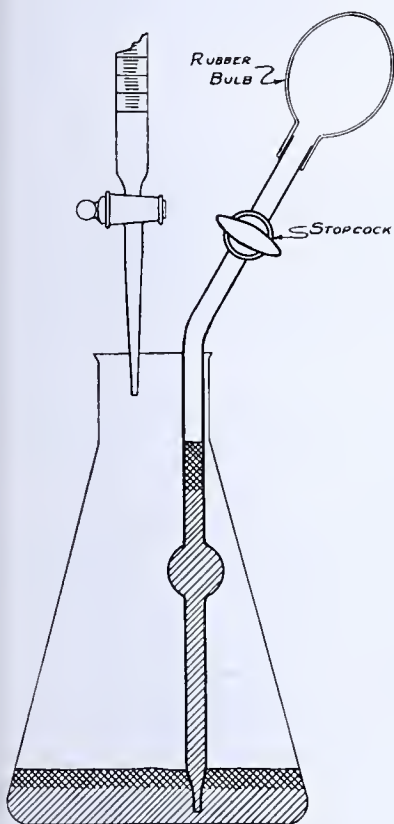
RECEIVED June 19, 1935.

The correction of temperature to the Kelvin scale is taken care of in the charts, so that Centigrade temperature is used.



Pipet for Titrating Dark-Colored Liquids in Two Phases

MILDRED M. HICKS-BRUUN AND LAWRENCE W. CLAFFEY, Sun Oil Company Research Laboratory, Norwood, Pa.



IN THE petroleum and other industries it is often necessary to determine the free acidity as well as saponification numbers of dark-colored substances. As many of these substances have comparatively high melting points and are very little soluble in alcohol, in recent years it has become the practice to use a benzene-alcohol solution, both for titrations with aqueous alkali (1, 4), and as a saponification medium with caustic potash and subsequent titration with aqueous acid (5). In either case the addition of an aqueous solution to the benzene-alcohol mixture precipitates a second layer; the dark-colored substance re-

mains in the upper phase (the benzene-alcohol layer), while the acidic constituents and excess alkali remain in the aqueous alcoholic layer. Coburn (4) has pointed out that sodium chloride may be added to render the two-phase separation sharper.

Methods in which the benzene-alcohol solution is used are often helpful in the determination of the end point, and more-

over a top benzene layer serves to protect caustic alkali solutions from atmospheric carbon dioxide during titration. However, the top layer is often dense and black and refuses to remain intact during the necessary swirling of the flask in titration. Furthermore, after the two layers are broken it not only requires several minutes for them to separate again, but also it is difficult to determine the exact end point of a yellowish or reddish solution beneath a heavy black layer.

To meet this need a pipet was devised in this laboratory which materially aided the operator's ability to determine the end point. The pipet was made a convenient length to remain in the titration flask throughout the titration, and may be of clear glass or with a white background. From time to time, the stopcock was opened and a convenient depth of the liquid was sucked into its stem by means of the rubber bulb, after which the stopcock was closed. If a portion of the benzene layer entered the pipet, it rose to the top of the liquid. The color of the indicator could then be closely observed and the liquid returned to the flask by opening the stopcock and applying pressure to the bulb. In this manner the progress of the titration could be noted until a satisfactory end point had been reached.

Although there are several titration flasks with forms of sealed-in tubes, such as those of Bezenberger (3) and Baader (2), the pipet here described was found not only to be simpler and more effective, but also better adapted for the technic of saponification numbers. Many uncertainties in the end points of dark-colored solutions have been avoided by its use.

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RECEIVED February 12, 1936.

Errors in Microweighing Due to the Use of Lead Shot in Tares

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THE Kuhlman microbalance which is most highly recommended by Pregl and his followers is provided by the manufacturer, in accordance with Pregl's recommendations, with a numbered series of small tare bottles of various sizes, and about 50 grams of fine lead shot with which to prepare tares for the different vessels in which material may be weighed.

The writer had occasion to weigh small samples of material in relatively large glass weighing bottles (weighing about 6 grams) and, although the balance seemed to be working perfectly and the temperature fluctuations were not excessive, constant values could not be obtained. In one case a weighing differed from that of the previous day by nearly 50 γ .

The cause of the excessive variations was traced to the use of the lead shot which had been provided. As soon as the lead was discarded and broken glass substituted for it in the tares, the difficulty promptly disappeared and weighings became constant.

Calculations show that if 5 grams (0.37 cc.) of lead are used to balance a glass vessel (this quantity is not excessive since the balances have a capacity of 20 grams), the difference in the volumes of air displaced by the lead and the glass (taking

2.7 as the specific gravity of glass) is about 1.5 cc. This air, if dry at standard pressure and 25° C., would weigh 1.78 mg. Under actual conditions, however, the weight of this excess air displaced by the glass vessel will vary 6 γ per degree of temperature variation, 23 γ per cm. of barometric variation, and about 21 γ for the difference between dry and saturated air.

Users of microbalances have always attempted to work at as constant a temperature as possible. It is evident, however, that the errors due to temperature variation are greatly magnified by the use of lead shot. More serious is the barometric variation because changes of a centimeter or more in the barometric reading, which readily occur, may introduce a serious error if lead shot is used. The error due to humidity variation may easily be considerable under some conditions.

If one insists on using lead shot, he can record temperatures, barometric readings, and humidities and make suitable corrections, but it is vastly simpler to render all these corrections entirely unnecessary by discarding the lead shot and using tares made of the same material as the vessel to be weighed.

It is clear to the writer that manufacturers should supply somewhat larger tare bottles and glass beads (or possibly

aluminum shot) to use in them. In case heavier objects are being weighed, care should be taken to have the vessel and the tare made of the same material, since the difference even between quartz and glass is sufficient to introduce appreciable errors in case the vessels are relatively heavy. Though the writer has had no experience in this connection, it appears that the weighing of the absorption tubes used in carbon and hy-

drogen determinations must be subject to especially large variations when lead shot are used in the tares, because of the relatively heavy objects weighed. The use of weights instead of tares leads to the same needless errors unless the weights have the same density as the objects to be weighed.

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New Apparatus for Analytical Laboratories

Crucible Support for Desiccators, Graduated Cylinder, and Flask Cover

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AS A RULE desiccators are supplied without plate or other device for support of crucibles and, on account of the inflexibility and expense of porcelain plate supports, the time and ingenuity of the user are often consumed in the fabrication of makeshift substitutes of glass, pipestem, etc.

The crucible support, Figure 1, described in this article is designed for use in the regular 15-cm. (6-inch) Scheibler desiccator and will hold six No. 0 or 00 porcelain crucibles with covers or the same number of platinum crucibles of corresponding sizes.



FIGURE 1

The support is made of pure nickel wire with all intersections securely brazed. Long and continuous use of the support justifies the following claims: By adjusting the legs it is readily adapted to variations in the shapes of desiccators, is held firmly in position during any legitimate use of the apparatus, holds the crucibles securely, may be deformed slightly to accommodate crucibles of different sizes, allows unrestricted circulation of air, and is kept bright with a minimum expenditure of time and the use of a little fine steel wool.

GRADUATED CYLINDER. In those chemical operations where one has occasion to measure rapidly volumes of liquid reagents, solvents, etc., there is great need of a handy measuring cylinder of moderate capacity, one that is sufficiently accurate, not easily upset, sturdy in construction, and not readily broken.

The cylinder illustrated in Figure 2 has all these characteristics and has been used in the different laboratories with great satisfaction, particularly in quantitative analytical work. Whereas the tall, narrow, 100-ml. cylinder in regular use at present is characterized by great instability, generally resulting in breakage when tipped over unless protected by

some sort of shock absorber, this short, wide cylinder stands more firmly on the table, is more readily filled and emptied, has two lips for convenient pouring, has never broken when tipped over, is graduated both up and down, and allows volumes to be measured as accurately as in any other cylinder of the same diameter.

It is not recommended for work that should be done only by an accurately calibrated pipet, buret, or certified tall narrow cylinder, but when made according to the dimensions given it stands supreme as a general-purpose measuring cylinder of 100-ml. capacity.

FLASK COVER. Many times, particularly when corrosive liquids are being boiled in flasks, it is desirable to resort to some device for control of spattering, evaporation, prevention of free access of air, dust, etc. In the past small funnels, inverted porcelain crucible covers, and glass bulbs have been employed for this purpose and generally with unpleasant results, because the center of gravity of the miscellaneous covers is above the rim of the vessel being covered.

The cover as illustrated (Figure 3) is designed upon a new

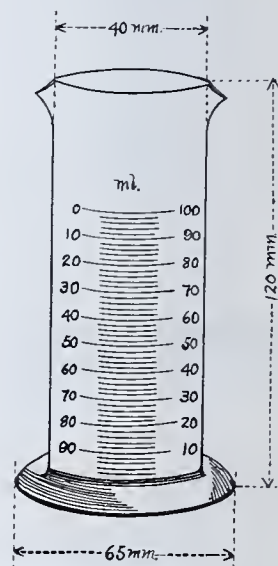


FIGURE 2

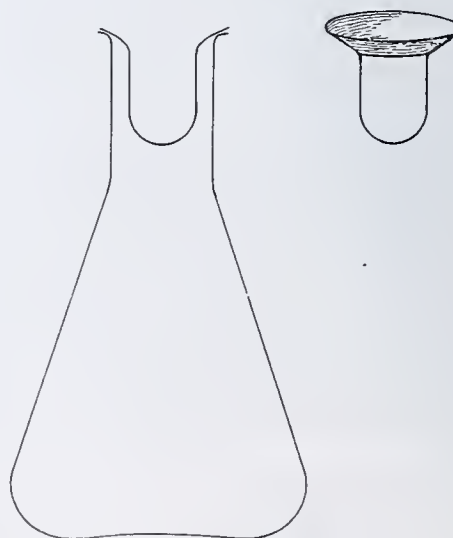


FIGURE 3

principle which places nearly its entire weight inside and below the rim of the vessel, so that it will remain securely in position even while the flask is being shaken.

Thus far three sizes of this cover have been successfully used and a careful inspection of the cut of the No. 3 size singly and in cross section as closing a 300-ml. Pyrex Erlenmeyer flask will show that it is capable of being used upon a wide

range of flask sizes—e. g., No. 1 may be used to close orifices from 11 to 19 mm. diameter, No. 2 those from 16 to 29 mm., and No. 3 those from 21 to 39 mm. Other sizes may be made if desirable.

The apparatus described in this article may be secured from Eimer & Amend, New York, N. Y.

RECEIVED March 19, 1936.

Condenser System for Fractional Distillation

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THE condenser described here has the advantages of flexibility and greater efficiency over the conventional types, being better insulated and providing an arrangement whereby almost any cooling medium may be used.

The illustrated apparatus has given great satisfaction in condensing vapors from fractional distillations. It greatly resembles the top of a Podbielniak column (2). An evacuated glass jacket, silvered for efficient heat insulation, surrounds the buret and condenser. The condenser itself is a metal cylinder fitting into the top of the glass jacket and is insulated from the glass by means of an asbestos cord. The cooling medium is run down into the condenser through tube *A* and escapes at *D*. Compressed carbon dioxide is very satisfactory, although liquid air or water may be used, according to the condensing range. The inner tube or condensing tube is of metal and contains a spiral strip extending down to the buret and dividing the tube into two compartments. Thus the vapors coming in at *B* pass down one side of the tube, condense, and fall into the buret. Displaced air must pass up the other side of the dividing strip and emerge at *C*, losing condensable vapors in transit. The metal condenser tube is connected to the glass buret by soldering to the platinized glass (1). This provides an air-tight seal between the metal and glass.

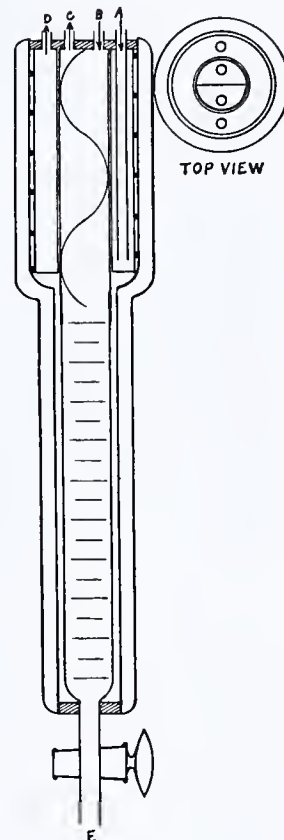
This apparatus is particularly useful in the distillation of gasoline. Lighter fractions and gases can be condensed by

use of a low-temperature cooling medium such as carbon dioxide or liquid air. The condenser is well adapted to vacuum distillation, the vacuum connection being made at *C* and liquid extracted at *E* by any of the conventional methods for extraction of liquids during vacuum distillation.

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RECEIVED March 9, 1936.



Dithizone as a Reagent for Dissolving and Determining Spray Residue Lead

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THE readiness with which dithizone (diphenylthiocarbazon) reacts with minute amounts of lead even when the lead is in such insoluble compounds as the sulfate and arsenate leads to the thought that this reagent might be made to assume a dual role in the analysis of spray residues for lead. The reagent might serve as the solvent for the removal of the lead from the analyzed fruits as well as in its ordinary capacity as colorimetric reagent. Were this possibility borne out by experimental investigation, and were there no other complicating factors, we should have an analytical method superior to any of those in present use in respect to speed and simplicity (1, 2).

After considerable investigation of this problem the writer desires to announce the following results and conclusions:

1. Lead is dissolved from the surface of fruits by a solution of dithizone in chloroform in the presence of an aqueous solution of potassium cyanide, ammonia, and citric acid. In order to effect a rapid and complete removal, a number of washings (two to six, depending on the amount of lead and the tenacity with which it is held) are necessary.

2. The dithizone color change due to the presence of lead occurs just as in the ordinary procedures. The contact with

the organic matter of the fruit skins does not seem to affect the reagent. As in other dithizone methods of spray residue analysis, there are no probable contaminants which will interfere in the lead determination. An occasional turbidity due to undissolved, suspended matter does not appear to be particularly detrimental to a close comparison of colors.

3. The multiple washings prevent the expected economy of time and materials and may decrease the accuracy and precision of a determination. Further work may reveal a way of increasing the solvent power of the dithizone solution and thereby the most serious obstacle to the success of this direct method of spray residue analysis will be removed.

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RECEIVED December 2, 1935. A more detailed discussion of the application of this method was presented under the title "A Field Method for the Estimation of Lead as Spray Residue" before the Division of Food and Agricultural Chemistry at the 90th Meeting of the American Chemical Society, San Francisco, Calif., August 19 to 23, 1935.

Detection of Lanthanum, Yttrium, and Ytterbium from Spark in Flame Spectra

O. S. PLANTINGA AND C. J. RODDEN, Washington Square College, New York University, New York, N. Y.

THE simplified spark in flame spectra method of Hultgren (1), previously reported by the authors (4), has been applied to the detection of lanthanum, yttrium, and ytterbium in rare earth salts. Lundegårdh (2) detected neodymium down to 0.01 M by a flame spectrum method, and Piccardi and Sberna (3) found limits of 0.01 per cent for lanthanum oxide and 0.001 per cent for yttrium oxide, using molecular flame spectra.

The method employed by the authors involves the visual spectroscopic examination, with a hand spectroscope, of a spark discharge in an ordinary gas flame in which the chloride, nitrate, or acetate solution of a sample is volatilized. The three elements studied were detected by the appearance of the following band heads in the spectra: for lanthanum, 4372, 4418, and 5600 Å.; for yttrium, the group 5892 to 6200 Å.; and for ytterbium, 5700 Å. The limit of detection, based on the dilution of a solution of each element of known strength, is in each case about 0.0001 M , although for concentrations lower than 0.001 M , the spectra flashed unsteadily. The limit of detection is affected by the presence of other rare earths or of large amounts of sodium. For example, a mixture of lanthanum and praseodymium chloride solutions,

in which the concentration of praseodymium was 1.5 M , showed a limit of detection of lanthanum only one-tenth of the value of pure lanthanum. A rough estimate of the amounts of the three elements may be made by examining the spectra of successive known dilutions of the sample until the bands disappear.

The method of detection outlined is economical and rapid, about 0.1 cc. of solution being used in a test requiring about a minute. The value of the method as applied to laboratory samples of the rare earths is illustrated by the examination of a sample of c. p. erbium which was found to contain 40 per cent of yttrium. The method has been successfully applied, in a few cases, in following the fractionation of rare earths.

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RECEIVED December 17, 1935.

Note to Authors

IN THE preparation of manuscripts authors should address themselves to specialists in their particular fields, rather than to the general reader. If the article describes a new method, the author should endeavor to tell the complete story, so that the reader will not have to wait for succeeding contributions or duplicate the unpublished tests in order to find out whether he can apply the method in his own work.

The following is suggested as a general outline to be followed in preparing analytical methods for this edition:

1. Preliminary statement or introduction, in which the need for the method should be stated, brief reference to other methods or literature given, etc.
2. Experimental
 - Outline of proposed method
 - Description of apparatus and reagents
 - Procedure
 - Data
 - Interfering substances or conditions
 - Concentration range through which the method is applicable
 - Accuracy of the method
 - Precision of the method
3. Discussion and summary

The author should state at the outset what the original features of the paper are. If it deals with a method of analysis, he should give some comparison with established methods in point of speed, applicability, accuracy, and cost. Extensive reviews of the literature should not be given and such references as are cited should be carefully checked. Incorrect references are inexcusable and cast doubts on the author's reliability. The theoretical considerations on which the method is based should be clearly set forth.

In the experimental part, previously published or well-known procedures which have been followed should only be designated or references given to them. If, however, the method is new, the data upon which it is based should be presented but in no greater detail than is necessary to prove its soundness. New procedures should be clearly described, that readers can easily duplicate the work. Loose directions should be avoided, unless the author

knows that no possible harm can result from the most liberal interpretation that can be made of such expressions as "to the faintly acid solution," "wash the precipitate," "ignite," etc. If new or uncommon reagents are needed, the author should state their probable cost, where they can be purchased if rare, or how they can be prepared, if not on the market.

The author should distinguish carefully between precision and accuracy. Briefly but somewhat roughly stated, accuracy is a measure of degree of correctness; precision is a measure of reproducibility. The precision of a result does not necessarily have anything to do with its accuracy; it serves merely as a measure of the duplicability of the procedure in the hands of a given operator. No claim for accuracy should be made unless the author believes that he has satisfactorily established the correct result.

The author should be frank and define the limitations of the method. Tests dealing with the effects of foreign compounds should be made on mixtures in which the ratios of the compounds sought to the foreign compounds are varied and simulate conditions that are likely to be encountered in practice. If the author has made no such tests, he should state that he has no knowledge of the effects of foreign substances. It is desirable that possible applications of methods should be stated.

A summary or prefatory abstract should acquaint the reader with the main points of the article. This should give concisely where possible the substances determined, nature of material to which determination is applicable, interfering substances, range of concentration to which method is applicable, whether or not a sensible constant error is involved—that is, the accuracy of the method—and its precision. Either the summary or the prefatory abstract is so often used by abstractors that the author may well spend considerable time in their preparation, in order to be certain that proper emphasis is given to the main features of the contribution.

Our "Suggestions to Authors" is available to those unfamiliar with the form of manuscript and illustrations preferred by INDUSTRIAL AND ENGINEERING CHEMISTRY.

INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

Report of Committee on Analysis of Commercial Fats and Oils, American Chemical Society

W. H. IRWIN, R. W. BAILEY, T. C. LAW, C. P. LONG, H. J. MORRISON, M. L. SHEELY, L. M. TOLMAN,
H. P. TREVITHICK, AND J. J. VOLLERTSEN

FOR the past two or three years, the reports of the Committee on Analysis of Commercial Fats and Oils have been progress reports with very few recommendations for adoption of methods. This has been due largely to the fact that it has been impossible for many laboratories to undertake coöperative work and it has been the policy of the committee not to accept the work of others but to base its recommendations on actual work of the committee. The committee is therefore happy this year to be able to report that its activities and the coöperative results on several lines of work warrant the recommendation to the SOCIETY of the adoption of several methods.

During the year the committee undertook the study of:

1. Modification of the Wiley melting point.
2. The thiocyanogen method as modified and used in the Procter & Gamble Laboratories.
3. The modified Twitchell method for the separation of liquid and solid fatty acids.
4. The detection of foreign fats containing tristearin in unhydrogenated pork fats.
5. Further work on the development of more satisfactory color standards for the committee's present standards.

WILEY MELTING POINT. In the case of the Wiley melting point, it was found necessary to draw the details of the method considerably closer, particularly as to the size of the pellet, the method of chilling, and the observance of the end point at which the pellet becomes a sphere. The latest modification was studied by the members of the committee, and coöperative results, in the opinion of the committee, warrant the recommendation for the adoption of this method as an official method of the SOCIETY.

THIOCYANOGEN METHOD. Many members of the SOCIETY are using, and have been using for a number of years, the thiocyanogen value determination and have found it very useful in calculating the various glycerides present in fat mixtures. However, there is not, at the present time, included in the methods of the SOCIETY a method for the determination of this value. As a part of the study on liquid and solid fatty acids, the committee used the method given below and the results were so consistently good that the committee feels justified in recommending it for the adoption of the SOCIETY at this time.

TWITCHELL METHOD. For a number of years the committee has been studying various methods of separation of liquid and solid fatty acids, but this year, at the suggestion of Mr. Long, it was decided to concentrate on the Twitchell method as modified and used in the Procter & Gamble Labora-

tories. The coöperative results which are appended to this report indicate extremely good agreement in the several laboratories on three separate sets of results on the same sample, and also excellent agreement between the coöperating laboratories on the same sample. In view of the good agreement on all of the figures reported, the committee recommends the adoption of the modified Twitchell method, as corrected by the use of the iodine and thiocyanogen values of the solid acids, as an official method of the SOCIETY.

It is further pointed out that the constituent fatty acids, with the exception of a distinction between oleic and isoöleic acid, may be calculated from the thiocyanogen value and the iodine value of the mixed fatty acids in accordance with the formula included in the method.

The committee's recommendation of the modified Twitchell method as corrected is based on the fact that, if it is desired to determine the isoöleic acid, it is necessary to make the solid acid separation.

The committee proposes to continue the work on liquid and solid acids, studying the Baughman-Jamieson modification for which some advantages are claimed.

DETECTION OF FOREIGN FATS CONTAINING TRISTEARIN IN UNHYDROGENATED PORK FATS. There are two methods at the present time given by the Association of Official Agricultural Chemists for the detection of tristearin in lard. In the first method, the fat is dissolved in ethyl ether and in the second acetone is the solvent used. There have been many complaints that it is impossible to get a satisfactory crop of crystals by the first method, and this is confirmed by the laboratories of the individual members of this committee. The committee, therefore, undertook the study of the second method described in the methods of the A. O. A. C. in which acetone is used as the solvent. The results indicate that a pure product may, in some instances, be condemned as adulterated if the conclusion is based on the results of the melting point of the glycerides only. The committee found, however, that if the method is carried through to determine the Bomer number, results appear satisfactory. The committee therefore recommends the adoption of the A. O. A. C. method as modified but deleting the sentence, "A melting point below 63° is regarded as evidence of adulteration, and a melting point below 63.4° is regarded as suspicious."

Tolman and Robinson (2) have pointed out that this method is not applicable to hydrogenated pork fats.

COLOR STANDARDS OF THE COMMITTEE. About 3 years ago, Mr. Doherty of Lever Brothers suggested a change in the chemicals used for the preparation of the committee's stand-

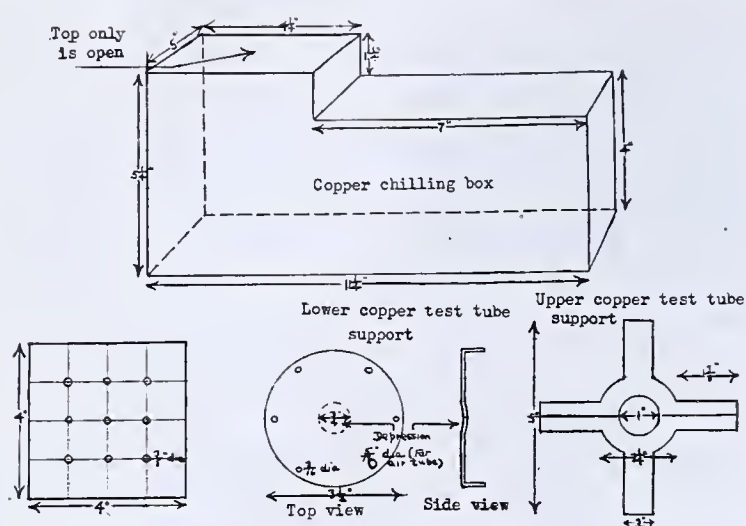


FIGURE 1. WILEY MELTING POINT APPARATUS

Lower copper test tube support is perforated to give proper air distribution for agitation.

Each arm of test tube support is bent at the end perpendicular to the plane of diagram in lower right-hand corner. Extension is 1.25 cm. (0.5 inch).

Lower left-hand corner, copper or brass plate, 3.2 mm. thick.

ards, one of the principal ones being uranyl chloride. The claim, which the committee agrees is sound, is that the inorganic salts recommended furnish more stable standards than the organic dyes dissolved in glycerol which have been used for a great many years. The committee found great difficulty in procuring a chemically pure supply of uranyl chloride; however, after rejection of five or six lots, a satisfactory supply was finally obtained. New standards have been prepared and are now in process of distribution to the users.

The change to inorganic salts in acid solution necessitated the use of ampules instead of the committee's regular tubes which are closed with a rubber stopper, because of the action of the solution on the stopper.

The committee expects to continue the study of methods which it thinks will be of interest to the SOCIETY during the coming year.

Modified Wiley Melting Point Method for Fats and Fatty Acids

APPARATUS. Chilling bath with heavy brass or copper plate drilled with holes 9.5 mm. in diameter and 3.2 mm. deep, for making disks (Figure 1).

Thermometer graduated to 0.1° C.

Beakers approximately 35 × 10 cm.

Test tubes 30 × 3.5 cm.

ALCOHOL-WATER MIXTURE. The specific gravity should be the same as that of the fat to be examined. Prepare by boiling, separately, water and 95 per cent alcohol for 10 minutes to remove the gases that may be held in solution. While still hot, pour the water into a test tube until it is almost half full. Nearly fill the test tube with the hot alcohol, pouring it down the side of the inclined tube to avoid too much mixing. If the alcohol is added after the water has cooled, air bubbles will make the mixture unfit for use.

DETERMINATION. Fill the chill bath with ice and water and place the copper or brass plate on the level surface of the bath. Fill the holes with the melted and filtered fat and allow to stand 2 or 3 hours before removing the disk from the plate. After the fat is thoroughly chilled, cut off the excess fat protruding above the level of the plate and either remove the disks and place in the cooler, or if no cooler is available allow to stand on the chill bath containing ice and water for a period of 2 or 3 hours until ready to make the determination.

Place a 30 × 3.5 cm. test tube containing the alcohol-water mixture in a tall 35 × 10 cm. beaker containing ice and water and leave until the mixture is cold. Then drop a disk of fat into the tube. It will sink immediately to a point where the density of the alcohol-water mixture is exactly equivalent to its own. Lower an accurate thermometer, which can be read to 0.1° C.,

into the test tube until the bulb is just above the disk. In order to secure an even temperature in all parts of the alcohol-water mixture around the disk, stir gently with the thermometer. Slowly heat the water in the beaker, constantly stirring it by means of an air blast or other suitable device.

When the temperature of the alcohol-water mixture rises to about 6° C. below the melting point of the fat, the disk of fat begins to shrivel and gradually rolls up into an irregular mass. Lower the thermometer until the fat particle is even with the center of the bulb. Rotate the thermometer bulb gently and so regulate the heat that about 10 minutes are required for the last 2° C. increase in temperature. As soon as the fat mass becomes spherical, read the thermometer. Remove the tube from the bath and again cool. Place in the bath a second tube containing the alcohol-water mixture. The test tube is of sufficiently low temperature to cool the bath to the desired point. After the first or preliminary determination, regulate the temperature of the bath so as to obtain a maximum of about 1.5° above the melting point of the fat under examination.

If the edge of the disk touches the sides of the tube, make a new determination. Run triplicate determinations. The second and third results should agree closely.

Determination of Thiocyanogen Number

REAGENTS. Lead thiocyanate, anhydrous glacial acetic acid, and bromine.

PREPARATION OF LEAD THIOCYANATE. Dissolve 250 grams of the finest c. p. neutral lead acetate $[\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}]$ in 500 cc. of distilled water. Dissolve likewise 250 grams of c. p. potassium thiocyanate in 500 cc. of water. Add the lead acetate solution to the potassium thiocyanate solution slowly and with stirring. Filter off the precipitated lead thiocyanate on a Büchner funnel and wash successively with distilled water, alcohol, and ether. Dry the lead thiocyanate as much as possible by drawing air through it. Remove from the funnel and dry on a watch glass in a phosphorus pentoxide desiccator for 8 to 10 days before using. This lead thiocyanate should be a greenish or yellowish white crystalline material; if it is at all discolored it must be discarded. Precipitated lead thiocyanate may be kept for a period not exceeding 2 months.

PREPARATION OF ACETIC ACID. Acetic acid is conveniently and suitably dehydrated by refluxing with acetic anhydride. In a 3-liter Florence flask, with a large test tube set in the neck and through which cold water is passed to serve as a condenser, are placed 2 liters of c. p. glacial acetic acid (99.5 to 100.0 per cent) and 100 cc. of acetic anhydride (90 to 100.0 per cent). This mixture is refluxed over an oil bath for 3 hours at approximately 135° C. After the anhydrous acid has cooled to room temperature, it should be placed in cleaned and dried glass-stoppered bottles.

PREPARATION OF AN 0.2 N SOLUTION OF THIOCYANOGEN. For the preparation of 1 liter of solution, suspend 50 grams of the dry lead thiocyanate in 500 cc. of anhydrous acetic acid; dissolve 5.1 cc. of the c. p. bromine in another 500 cc. of acid. Two glass-stoppered acid bottles of 2 or 3 liters capacity, which have previously been thoroughly cleaned and dried, should be used for this purpose. Add the bromine solution to the lead thiocyanate suspension slowly, in small portions, and shake vigorously, between each addition, until the solution is completely decolorized. After all the bromine has been added, allow the precipitated lead bromide and the excess lead thiocyanate to settle out, then filter the solution as rapidly as possible. A 13-cm. Büchner funnel and qualitative filter paper together with two 2-liter pressure flasks are used for the filtration. They are previously dried for 1 hour at 105° C. The entire solution is filtered by suction into the one flask, when the funnel, containing the paper and some cake, is transferred to the second flask and the solution refiltered. It should be perfectly clear upon the second filtration. The solution should be stored in glass-stoppered brown bottles and kept in a cool place, 15.56° to 21.11° C. (60° to 70° F.). If it is convenient, the following method for the preparation of the thiocyanogen solution can be used to advantage. Suspend 50 grams of the dry lead thiocyanate in 600 cc. of anhydrous acetic acid in a round-bottomed 2-liter flask, equipped with a mechanical stirrer and a dropping tube. Slowly add with agitation 5.1 cc. of c. p. bromine suspended in 200 cc. of dry acid in the dropping tube. The acetic acid-bromine solution should be added at a rate such that the liquid in the reaction flask remains only faintly tinged with brown. When the entire bromine-acetic acid solution has been added, the dropping tube is rinsed out with an additional 200 cc. of the dry acid which is added immediately to the reaction mixture. When the bromine has all reacted, as indicated by the color of the reaction mixture, the agitation is ceased, the precipitated lead bromide allowed to settle, and the thiocyanogen solution filtered as described above.

TABLE I. SUMMARY OF RESULTS ON LIQUID AND SOLID ACIDS

Component Acids	Modified Twitchell				Modified Twitchell Corrected				Thiocyanogen									
	1	2	3	Av.	1	2	3	Av.	1	2	3	Av.						
Values Determined by M. L. Sheely																		
Oleic acid	47.4	61.5	47.9	61.4	47.0	60.9	61.3	44.7	58.4	45.9	58.4	45.3	58.8	58.5	57.9	58.3	58.8	58.3
Isooleic acid	14.1		13.5		13.9			13.7		12.5		13.5						
Linoleic acid		10.2		10.2		10.5	10.3		11.7		11.7		11.5	11.6	12.0	11.8	11.5	11.8
Saturated acids		28.3		28.4		28.6	28.4		29.9		29.9		29.7	29.9	30.1	29.9	29.7	29.9
Values Determined by J. J. Vollertsen																		
Oleic acid	47.1	61.0	47.3	61.1	47.0	61.1	61.1	45.2	58.4	44.3	57.0	45.4	58.2	57.9	58.2	60.4	58.8	59.1
Isooleic acid	13.9		13.8		14.1			13.2		12.7		12.8						
Linoleic acid		10.4		10.3		10.4	10.4		11.6		12.3		11.6	11.8	11.8	10.7	11.5	11.3
Saturated acids		28.7		28.6		28.5	28.6		30.0		30.7		30.2	30.3	30.0	28.9	29.7	29.5
Values Determined by C. P. Long																		
Oleic acid	44.0	60.2	49.3	63.8	44.8	59.5	61.2	40.0	55.8	44.5	56.0	42.0	56.6	56.1	56.0	56.6	57.2	56.6
Isooleic acid	16.2		14.5		14.7			15.8		11.5		14.6						
Linoleic acid		11.0		9.2		11.3	10.5		13.2		13.1		12.8	13.0	13.9	12.8	12.5	13.1
Saturated acids		28.8		27.0		29.2	28.3		31.0		30.9		30.6	30.8	30.1	30.6	30.3	30.3
Values Determined by W. H. Irwin																		
Oleic acid	48.6	62.5	48.0	62.2	48.4	62.0	62.2	45.0	58.6	46.0	58.8	46.2	59.0	58.8	59.0	59.0	59.5	59.2
Isooleic acid	13.9		14.2		13.6			13.6		12.8		12.8						
Linoleic acid		9.8		10.1		10.0	10.0		11.7		11.6		11.5	11.6	11.5	11.5	11.3	11.4
Saturated acids		27.7		28.0		28.0	27.9		29.7		29.6		29.5	29.6	29.5	29.5	29.2	29.4

TABLE II. LIST OF DETERMINED VALUES FOR LIQUID AND SOLID ACIDS

	C. P. Long			J. J. Vollertsen			M. L. Sheely			W. H. Irwin		
	1	2	3	1	2	3	1	2	3	1	2	3
Iodine number of sample	70.8	70.8	70.7	70.7	70.8	70.7	70.8	70.8	70.8	70.6	70.7	70.6
Thiocyanogen number of sample	59.4	59.6	59.8	60.7	60.2	60.0	59.3	59.1	59.3	60.6	60.6	60.8
Iodine number of fatty acids	74.1	74.1	74.0	73.7	73.7	73.6	73.8	73.8	73.8	73.9	73.9	73.9
Thiocyanogen number of fatty acids	62.2 ^a	62.5 ^a	62.7 ^a	63.0	64.0	63.2	62.9	63.1	63.3	63.5 ^a	63.5 ^a	63.7 ^a
Solid fatty acids (Twitchell), %	45.0	41.5	43.9	42.5	42.4	42.6	42.4	41.9	42.5	41.6	42.2	41.6
Iodine number of solid fatty acids	32.3	31.5	30.2	29.2	29.4	29.8	29.9	29.0	29.4	30.0	30.1	29.5
Thiocyanogen number of solid fatty acids	31.9	28.2	30.1	28.6	28.2	28.4	29.4	28.3	29.0	29.7	28.7	28.6

^a Calculated from thiocyanogen value of glycerides.

DETERMINATION OF THE THIOCYANOGEN NUMBER (1). Weigh 0.1 to 0.3 gram of oil accurately into a dry 125-cc. glass-stoppered Erlenmeyer flask. Add from a pipet 25 cc. of thiocyanogen solution and allow to stand for 24 hours in the dark. The storage place should be from 18.33° to 21.11° C. (65° to 70° F.) in temperature and should not exceed 21.11° C. (70° F.) for any length of time. The size of the sample is governed largely by the expected thiocyanogen absorption. The excess thiocyanogen should be at least 100 per cent and preferably less than 150 per cent of the amount absorbed by the oil, although a greater excess seems to do no harm. At the end of 24 hours, 1 gram of dry powdered potassium iodide is added and the flask swirled rapidly for 2 minutes. It is advisable to agitate the blank determination for 3 minutes. (Mechanical agitation such as is employed for iodine values is found very satisfactory for thiocyanogen values.) Then add 30 cc. of distilled water and titrate the liberated iodine with 0.1 N sodium thiosulfate, using starch as an indicator. At least three blanks should be run with the samples. The solution should also be titrated at the beginning of the 24-hour period. If the drop is more than 0.2 cc. on the blank titrations, the solution is decomposing too rapidly and erratic and low figures will be the result.

$$T.V. = \frac{(\text{blank titration} - \text{titration of sample}) \times (\text{normality of Na}_2\text{S}_2\text{O}_3) \times 12.69}{\text{weight of sample}}$$

or the calculation may be expressed as follows:
$$T.V. = \frac{(\text{blank titration} - \text{titration of sample}) \times \text{Na}_2\text{S}_2\text{O}_3 \text{ factor (I.V.)} \times 100}{\text{weight of sample}}$$

when the sodium thiosulfate factor (I.V.) is expressed as grams of I₂ per cc.

IODINE NUMBER DETERMINATION. An iodine number must be determined on the fat by the regular Wijs method.

CALCULATION OF FAT COMPOSITION. The following calculations are to be used when the iodine number and thiocyanogen number are determined on the fat directly and it is desired to express the percentages of the various acids as glycerides. In these formulas no unsaturation greater than linoleic is assumed to be present.

I.V. = iodine number of the oil
T.V. = thiocyanogen number of the oil
S.G. = per cent of saturated glycerides
O.G. = per cent of oleic glycerides
L.G. = per cent of linoleic glycerides

Then

$$L.G. = 1.154 (I.V. - T.V.)$$

$$O.G. = 1.162 (2T.V. - I.V.)$$

$$S.G. = 100\% - (L.G. + O.G.)$$

When the iodine number and thiocyanogen number have been determined directly or indirectly on the free fatty acids of the oil, the percentages of the various acids may be determined, not as glycerides but as per cent of acid, in the following manner:

$$\% L.A. = 1.104 (I.V. - T.V.)$$

$$\% O.A. = 1.112 (2T.V. - I.V.)$$

$$\% S.A. = 100\% - \% (L.A. + O.A.)$$

NOTES AND OBSERVATIONS. All glassware and chemicals used in the preparation or handling of thiocyanogen solutions must be absolutely free from water. The glassware should be scrupulously cleaned with cleaning solution, water, alcohol, and ether and then dried for 1 to 2 hours in an oven at 105° C.

The thiocyanogen solution should not be exposed to air, heat, or light for any length of time.

The 0.2 N thiocyanogen solution cannot be used after its decomposition exceeds 0.2 cc. of 0.1 N sodium thiosulfate for 25 cc. over a period of 24 hours. This rate of decomposition should not be exceeded in less than 7 days.

Liquid and Solid Fatty Acids: Modified Twitchell Separation

PREPARATION OF MIXED FATTY ACIDS. Saponify in a 600-cc. beaker about 25 grams of the melted oil sample with about 15 grams of potassium hydroxide dissolved in a small amount of water and 25 cc. of 95 per cent alcohol. Bring to dryness on steam bath or hot plate. (Care should be taken not to burn the soap.) Add to the soap about 200 cc. of distilled water, heat on steam bath until soap is dissolved, and add concentrated hydrochloric acid while stirring until soap is completely broken up. A small strip of litmus will show when mixture has been acidulated. Heat the solution containing curds of fatty acids on steam bath or hot plate until they, together with the entire contents of beaker, will pour freely into a 500-cc. separatory funnel. Transfer should be aided with 100 to 150 cc. of ethyl ether. Fatty acid-ether solution must then be washed free of acid with distilled water. Usually three washings are sufficient, but tests of wash water with methyl orange indicator should be made. Separation of water from fatty acid-ether solution should be made as close as possible to ensure absence of water in the mixed fatty acid sample. After washing free of acid, filter fatty acid-ether solution through paper into a 250-cc. Soxhlet. Evaporate all trace of ether on steam bath under a current of inert gas. (Use precaution to prevent oxidation of fatty acid.)

SEPARATION OF SOLID FROM LIQUID FATTY ACIDS (3). From the ether-free mixed fatty acids, weigh accurately into a 250-cc.

TABLE III. DETAILED DATA OF COÖPERATIVE WORK ON LIQUID AND SOLID FATTY ACIDS

	—C. P. Long—			—J. J. Vollertsen—			—W. H. Irwin—			—M. L. Sheely—		
	1	2	3	1	2	3	1	2	3	1	2	3
Thiocyanogen Analyses												
Iodine number of sample	70.8	70.8	70.7	70.7	70.8	70.7	70.6	70.7	70.6	70.8	70.8	70.8
Thiocyanogen number of sample	59.4	59.6	59.8	60.7	60.2	60.0	60.6	60.6	60.8	59.3	59.1	59.3
Oleic glycerides, %	55.8	56.2	56.8	58.9	57.6	58.1	58.8	58.7	59.3	56.3	55.2	55.5
Linoleic glycerides, %	13.2	12.9	12.6	11.5	12.2	12.3	11.5	11.6	11.3	13.0	13.5	13.3
Saturated glycerides, %	31.0	30.9	30.6	29.6	30.2	29.6	29.7	29.7	29.4	30.7	31.3	31.2
Twitchell Analyses (P. & G.)												
Iodine number of mixed fatty acids	74.1	74.1	74.0	73.7	73.7	73.6	73.9	73.9	73.9	73.8	73.8	73.8
Iodine number of solid fatty acids (detd.)	32.3	31.5	30.2	29.2	29.4	29.8	30.0	30.1	29.5	29.9	29.0	29.4
Iodine number of unsaturated fatty acids (calcd.)	104.1	101.5	104.5	103.5	103.4	103.0	102.3	102.7	102.6	102.9	103.0	103.3
Solid fatty acids (detd.), %	45.0	41.5	43.9	42.5	42.4	42.6	41.6	42.2	41.6	42.4	41.9	42.5
Liquid fatty acids (calcd.), %	55.0	58.5	56.1	57.5	57.6	57.4	58.4	57.8	58.4	57.6	58.1	57.5
Saturated fatty acids (calcd.), %	28.8	27.0	29.2	28.7	28.6	28.5	27.7	28.0	28.0	28.3	28.4	28.6
Isooleic acid (calcd.), %	16.2	14.5	14.7	13.8	13.8	14.1	13.9	14.2	13.6	14.1	13.5	13.9
Linoleic acid (calcd.), %	11.0	9.2	11.3	10.4	10.3	10.4	9.8	10.1	10.0	10.2	10.2	10.5
Oleic acid (calcd.), %	44.0	49.3	44.8	47.1	47.3	47.0	48.6	47.8	48.4	47.4	47.9	47.0
Twitchell and Thiocyanogen Analyses, Calculated by Sheely's Method												
Iodine number of solid fatty acids	32.3	31.5	30.2	29.2	29.4	29.8	30.0	30.1	29.5	29.9	29.0	29.4
Thiocyanogen number of solid fatty acids	31.9	28.2	30.1	28.6	28.2	28.4	29.7	28.7	28.6	29.4	28.3	29.0
Solid fatty acids (uncorrected), %	45.0	41.5	43.9	42.5	42.4	42.6	41.6	42.2	41.6	42.4	41.9	42.5
Liquid fatty acids (uncorrected), %	55.0	58.5	56.1	57.5	57.6	57.4	58.4	57.8	58.4	57.6	58.1	57.5
Unsaturated acids by (SCN) ₂ , %	69.0	69.1	69.4	70.4	69.8	70.4	70.3	70.3	70.6	70.1	70.1	70.3
Linoleic acid in solid fatty acids, %	0.2	1.5	0.0	0.3	0.6	0.7	0.2	0.6	0.4	0.2	0.3	0.2
Oleic acid in solid fatty acids, %	15.8	11.5	14.6	13.2	12.7	12.8	13.6	12.8	12.8	13.7	12.5	13.5
Solid saturated acids, %	29.0	28.5	29.3	29.0	29.1	29.1	27.8	28.7	28.4	28.5	29.1	28.8
Saturated acids in liquid acids, %	2.0	2.4	1.3	1.0	1.6	1.1	1.8	0.9	1.1	1.4	0.8	0.9
Total saturated acids, %	31.0	30.9	30.6	30.0	30.7	30.2	29.7	29.7	29.4	29.9	29.9	29.7

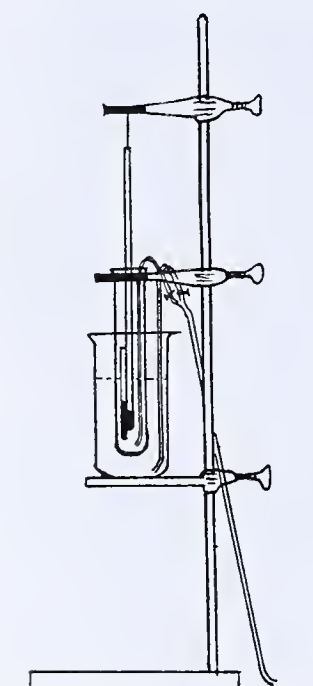


FIGURE 2. APPARATUS FOR DETERMINATION OF MELTING POINT

beaker a sample that will give approximately 1.2 ± 0.3 grams of solid fatty acids. The sample weight should never exceed 5 grams. Weigh 1.5 grams of powdered lead acetate into another beaker. Add to each about 50 cc. of 95 per cent alcohol, cover with watch glasses, and bring both to boil on hot plate or steam bath. Transfer the hot alcoholic lead acetate to the alcoholic fatty acids, stirring continually with a glass stirring rod which may be left in sample to aid later in filtration. Cool to room temperature and place in ice bath at 15°C . for 2 hours or in ice box at approximately 15°C . overnight. Filter through 7.5-cm. (3-inch) Büchner funnel which has filter paper cut to fit snugly. Suction should be used to aid filtration. Use 200 cc. of 95 per cent alcohol cooled to 15°C . to transfer lead soaps from beaker to Büchner and in washing. After alcohol has filtered from the lead soaps, transfer them quantitatively back to the original beaker, using about 100 cc. of warm 95 per cent alcohol to aid the transfer. Make 0.5 per cent

acetic acid with glacial acetic acid.

Before discarding filtrate, make a test for excess lead acetate by adding a few drops of concentrated sulfuric acid to about 50 cc. of the filtrate. Absence of cloudiness shows the sample of fatty acids was too large and present sample is of no value; therefore, it will be necessary to weigh a smaller sample of mixed fatty acids and apply the same procedure. If there is an excess of lead acetate, continue with present sample by bringing it to a boil on hot plate, stirring occasionally to assure solution of the lead soaps. Cool to room temperature, then in ice bath at 15°C . for 2 hours or in ice box overnight. Filter through Büchner, using suction and 200 cc. of 15°C . 95 per cent alcohol as in first filtration. After lead soaps are drawn free of alcohol, transfer them quantitatively to original beaker, using ethyl ether to aid (about 75 cc.). Break up lead soaps by adding 20 cc. of 1 to 3 nitric acid. Transfer to a 500-cc. separatory funnel, using ethyl ether to aid. An extra 5-cc. portion of 1 to 3 nitric acid may be used to advantage in removing the last trace of sample from the beaker. Wash ether with distilled water until neutral to methyl orange. Transfer ether to a tared 150-cc. Soxhlet and wash all traces of solid fatty acids into the Soxhlet with ether. Evaporate ether on steam bath under a current of inert gas. Dry in an oven at 103°C . for 1 hour, remove, cool, and weigh. See that no water is in sample. It is well to be sure of constant weight by returning to oven a second time for 30 minutes.

$$\frac{\text{Weight of solid acids} \times 100}{\text{Weight of sample}} = \text{per cent of solid fatty acids}$$

IODINE AND THIOCYANOGEN DETERMINATIONS OF SEPARATED SOLID ACIDS. Determine these values by the regular Wijs method for iodine number and by the thiocyanogen value method recommended by this committee.

From these values, calculate the component acids according to the following formulas:

Let $I.N.$ = iodine number of solid acids

$T.N.$ = thiocyanogen number of solid acids

C = per cent of solid acids uncorrected

D = per cent of liquid acids uncorrected

E = per cent of unsaturated acids by thiocyanogen method

Linoleic acid in solid acids = $1.104 (I.N. - T.N.) \times C = L.A.$

Oleic acid in solid acids = $1.112 (2 T.N. - I.N.) \times C = O.A.$

Then solid saturated acids = $C - (L.A. + O.A.)$

Then saturated acids in liquid acids = $D + (L.A. + O.A.) - E$

Total saturated acids = per cent of solid acids (as found) - (oleic in solid acid + linoleic in solid acid) + saturated acids in liquid acids

Total unsaturated acids = $100 - \text{total saturated acids}$

$$\text{Total oleic acid} = \frac{(\text{total unsaturated acids} \times 181) - I.V.M.F.A. \times 100}{91} \quad (1)$$

Total linoleic acid = total unsaturated acids - total oleic acid

Formula 1 is derived as follows:

Y = total unsaturated acids

X = total oleic + isooleic acids

$Y - X$ = total linoleic acid

Z = iodine value of mixed fatty acids

90 = iodine value of oleic acid

181 = iodine value of linoleic acid

$$90X + 181(Y - X) = 100Z$$

$$X = \frac{181Y - 100Z}{91}$$

Iodine and thiocyanogen values for mixed fatty acids can be computed from the corresponding values of the neutral glycerides (under 1 per cent free fatty acids) by making use of a factor derived from the molecular weight of the glycerides. The average molecular weight of the glycerides can be determined by use of the saponification number.

The calculations of constituent acids are based on the assumption that no acids more unsaturated than linoleic are present.

Detection of Foreign Fats Containing Tristearin in Unhydrogenated Pork Fats

A. O. A. C. METHOD MODIFIED. Weigh 5 grams of the filtered fat into a glass-stoppered cylinder graduated to 25 cc. and add warm acetone until the 25-cc. mark is reached. Shake the cylinder until the contents are thoroughly mixed and allow to stand where a temperature of 30°C . is maintained. After 18 hours, remove the cylinder and carefully decant the supernatant

acetone solution from the crystallized glycerides which are usually found in a firm mass at the bottom of the cylinder. Add warm acetone in 3 portions of 5 cc. each from a small wash bottle, taking care not to break up the deposit while washing, and decant the first 2 portions. Actively agitate the third portion in the cylinder, and by a quick movement transfer with the crystals to a small filter paper. Using the wash bottle, wash the crystals with 5 successive small portions of the warm acetone, and remove the excess acetone by suction. Transfer the paper with its contents to a suitable place, spread out, and break up by gentle pressure any large lumps of the glycerides. When dry, thoroughly comminute the mass and determine the melting point of the crystals in a closed 1-mm. tube as follows, using apparatus as shown in Figure 2.

Heat the water in the beaker rapidly to about 55° C. and maintain this temperature until the thermometer carrying the melting point tube registers 50° to 55° C.; then heat again and carry the temperature of the outer bath somewhat rapidly to 67° C. Remove the burner. The melting point is reached when the fused substances become perfectly clear and transparent. A dark background placed about 10 cm. (4 inches) from the apparatus will be helpful.

After determining the melting point, transfer the crystallized

glycerides to a 50-cc. beaker, add 25 cc. of approximately 0.5 N alcoholic potassium hydroxide, and heat on a steam bath until saponification is complete. Pour the solution into a separatory funnel containing 200 cc. of water, acidify, add 75 cc. of ether, and shake. Draw off the acid layer and wash at least 3 times with water. Transfer the ether solution to a clean, dry 50-cc. beaker, drive off the ether on a steam bath, and finally dry the acids at 100° C. After about 2 hours, determine the melting point as directed above. If the melting point of the glycerides, plus twice the difference between the melting point of the glycerides and the melting point of the fatty acids, is less than 73° C., the pork fat is regarded as adulterated.

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Indicators

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TWO years ago a symposium on indicators was held by the Division of Physical and Inorganic Chemistry, and it is questionable whether anything can be added to what was said at that time. This paper will consider the future development of the subject.

Virtually all the indicators used in volumetric analysis, and in the determination of pH, are organic substances. In classifying indicators we may distinguish (1) acid-base indicators, (2) oxidation-reduction indicators, (3) adsorption indicators, and (4) specific indicators for ion-combination reactions.

Acid-Base Indicators

An acid-base indicator involves the conjugated system $I_a \rightleftharpoons I_b + H^+$, I_a being the donor of the proton and I_b the acceptor.

A great many indicators with acid-base properties are available at present, and there is no pressing need of developing new ones as far as volumetric analysis is concerned. The case is different with regard to the determination of pH. At the outset it should be made clear what we mean by pH. Strictly speaking, the pH is the negative logarithm of the hydrogen-ion concentration. However, in the colorimetric determination of pH we usually compare the color of the test solution containing indicator with that of the indicator in a buffer solution whose hydrogen-ion activity has been determined potentiometrically. Neglecting the salt error, we say that equicolored solutions of the indicator have the same pH, or the same hydrogen-ion activity. In some cases it would be of importance to know the hydrogen-ion concentration as well.

Quantitatively the following relations exist:

$$\frac{(aH^+)(aI_b)}{(aI_a)} = \frac{(cH^+)(cI_b)f_H f_{I_b}}{(cI_a)f_{I_a}} = K_I \quad (1)$$

K_I is the thermodynamic ionization constant of the indicator—i. e., its value is constant, independent of the ionic strength. From Equation 1 it is seen that

$$(cH^+) = K_I \frac{(cI_a)}{(cI_b)} \frac{f_{I_a}}{f_H f_{I_b}} = \frac{(cI_a)}{(cI_b)} K_{I_c} \quad (2)$$

In a colorimetric pH determination $\frac{(cI_a)}{(cI_b)}$ is found experimentally. Hence when the "concentration ionization constant," K_{I_c} , is known (cH^+) can be calculated. The value of K_{I_c} varies with the ionic strength of, and the kind of ions in the solution, and with the type of indicator used.

From Equations 1 and 2 it is seen that

$$K_{I_c} = K_I \frac{f_{I_a}}{f_H f_{I_b}} \quad (3)$$

As a rule it is possible to determine K_{I_c} in an exact way for different salts as a function of the ionic strength. Such data can be tabulated and used when necessary. Ordinarily the method has a very limited application, since the concentrations of the various ions constituting the ionic strength are generally not known and in addition we may be dealing with complicated salt mixtures in which K_{I_c} is unknown.

Considering Equation 3, we can predict the order of magnitude of the change of K_{I_c} with varying ionic strength for different types of indicators. If I_a is a monovalent cation and I_b the corresponding uncharged indicator base, f_{I_a} represents the activity coefficient of the monovalent indicator cation, f_H that of the monovalent hydronium ion, and f_{I_b} that of the uncharged indicator base. At low ionic strengths f_{I_b} will be practically equal to unity, whereas f_{I_a} will be approximately equal to f_H , since I_a^+ and H^+ have the same charge. Therefore, we may expect that over a limited range of ionic strength from zero to a certain finite value $\frac{f_{I_a}}{f_H f_{I_b}}$ will remain

equal to 1 and K_{I_c} will remain constant and equal to K_I . Thus an indicator, the uncharged form of which is a base and the acid form of which is a monovalent cation, should be particularly suitable for the colorimetric determination of the hydrogen-ion concentration at low ionic strengths. At present such indicators are hardly used for pH work. The methoxy-triphenylcarbinols are brilliant indicators of the above type, but unfortunately they are not commercially available. From the foregoing, then, we may state that for the future development of the colorimetric method for the determination of the hydrogen-ion concentration, a system-

atic study should be made of the indicator properties of indicator dyes, the uncharged forms of which are bases.

The activity of the hydrogen ions can be determined potentiometrically. Although it is impossible to measure an individual ion activity in an exact way, it is possible to approach the value very closely. In hydrogen-ion work the data obtained with the hydrogen electrode are considered to be standard values, and the pH values of buffers used in colorimetric determinations have been found in this way.

Considering two solutions having hydrogen-ion activities of $(a\text{H}^+)_1$ and $(a\text{H}^+)_2$, which impart the same color to a certain indicator, it is found from Equation 1 that

$$\frac{(a\text{H}^+)_1}{(a\text{H}^+)_2} = \left(\frac{f_{I_a}}{f_{I_b}}\right)_2 : \left(\frac{f_{I_a}}{f_{I_b}}\right)_1 \quad (4)$$

since $\frac{cI_a}{cI_b}$ is the same in both solutions. The logarithm of the above ratio

$$\text{pH}_2 - \text{pH}_1 = \Delta\text{pH} = \log \left(\frac{f_{I_a}}{f_{I_b}}\right)_2 - \log \left(\frac{f_{I_a}}{f_{I_b}}\right)_1 \quad (5)$$

is usually called the salt error of the indicator, and is equal to the difference of the logarithms of the ratios of the activity coefficients of the acid and basic form of the indicator in both solutions. Assuming that the limiting Debye-Hückel expression holds, we find that $-\log f = 0.5 z^2 \sqrt{\mu}$ in which μ is the ionic strength and z the valence of the ion. In case I_a is an uncharged acid, I_b will be a monovalent anion. According to Equation 5

$$\Delta\text{pH} = -\log f_{I_{b_2}} + \log f_{I_{b_1}} = 0.5 \{ \sqrt{\mu_2} - \sqrt{\mu_1} \}$$

In case I_b is an uncharged base, I_a is a monovalent cation. Numerically the salt error will be the same as in the above case but will have the opposite sign:

$$\Delta\text{pH} = 0.5 \{ \sqrt{\mu_1} - \sqrt{\mu_2} \}$$

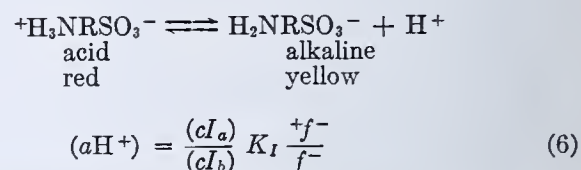
If I_a is a monovalent anion and I_b is a divalent anion, it is easily derived that

$$\Delta\text{pH} = 1.5 \{ \sqrt{\mu_2} - \sqrt{\mu_1} \}$$

Thus assuming that the limiting Debye-Hückel expression holds, it is found that the salt error is three times greater for the indicator whose acid form is a monovalent anion than for an indicator whose acid form is uncharged. Actually it is found that the salt error of the nitrophenols which are uncharged acids is of the order of three times smaller than that of the phthaleins and the sulfophthaleins, the acid form of the latter two types being a monovalent anion and the alkaline form a divalent anion. It may be expected that the salt error of the sulfophthaleins could be reduced materially by eliminating the sulfonic acid group. The benzeins so obtained behave as uncharged indicator acids and show brilliant color changes similar to those of the sulfophthaleins. Unfortunately, the benzeins are only extremely slightly soluble in water, and for this reason are unsuitable for colorimetric measurements in aqueous media. However, it should be possible to substitute for the sulfonic group another polar group which has no, or only very weak, electrolyte character, such as an amino group, an aliphatic hydroxyl group, etc. These substituted benzeins may be expected to have a sufficient solubility in water to be useful as indicators, they should have indicator constants of the same order as the corresponding sulfophthaleins and show similar bright color changes, but their salt error should be about three times smaller than that of the sulfophthaleins.

Finally it should be noted that the salt error could be re-

duced to zero if the activity coefficients of the acid and alkaline forms would change in the same manner with varying ionic strength. This case is approached with an indicator, the acid form of which is a hybrid (Zwitter) ion and the alkaline form a monovalent anion, as for example with methyl orange. The indicator equilibrium can be represented by the equation



Over a relatively wide range of ionic strengths $+f^-$ changes in the same way as f^- . Hence Equation 6 reduces to the following:

$$(a\text{H}^+) = \frac{(cI_a)}{(cI_b)} K_I \quad (7)$$

Therefore, in a search for indicators having a negligibly small salt correction at moderate ionic strengths, we should seek those substances, the acid or basic form of which is a hybrid ion of the above type. It thus appears that by a rational combination of organic and physico-chemical principles valuable additions to the existing list of pH indicators can be anticipated.

Oxidation-Reduction Indicators

Little, if any, application in volumetric analysis has been made of the brilliant researches by W. M. Clark and his coöperators and by L. Michaelis. They have provided us with a series of oxidation-reduction indicators of low oxidation potentials which should be useful in titrations with strong reducing agents, such as titanous, chromous, or stannous chlorides. From the oxidation potential of the constituent titrated, and that of the reducing agent, it is possible to calculate the potential at the equivalence point and the change of the potential in the vicinity of this point. Theoretically, therefore, it is possible to calculate the range of oxidation potentials in which that of an indicator must be located to be suitable. In the selection of the proper indicator upon such theoretical considerations, one should realize that in most cases the location of the equivalence potential of a titration depends upon the hydrogen-ion concentration and the ionic strength of the medium. Moreover, a specific effect of anions or cations upon the oxidation potential of the constituent titrated, or upon that of the reagent, or upon both, is frequently found, usually as a result of complex formation. Thus, the suitable range of oxidation potentials in which the color change must occur becomes a function of the medium. Considering oxidation-reduction indicators, it must be kept in mind that their oxidized and reduced forms as a rule are donors (acids) or acceptors (bases) of protons. Their oxidation potentials, therefore, are more or less complicated functions of the hydrogen-ion concentration of the solution, and in addition depend upon the ionic strength of the medium.

The above considerations are not of great practical consequence in cases where the jump in potential near the equivalence point is very pronounced, but they become of primary importance when the "useful range" of oxidation potentials becomes small. In the potentiometric titration of a mixture of oxidizing or reducing agents with widely different oxidation potentials, the concentration of each constituent is found from the successive breaks in potential which occur during the titration. It should be possible to substitute the potentiometric titration by a visual one if the proper indicators are available. It is particularly in these cases in which the above-

mentioned factors affecting the location of the equivalence potential and the oxidation potential of the indicator become of primary significance. A great deal of systematic research must be done before a successful application of oxidation-reduction potentials can be expected in differential titrations with strong reducing reagents.

The analytical researches have concentrated mainly upon oxidation-reduction indicators with relatively high oxidation potentials and have yielded important results. Until about ten years ago, when Knop proposed the use of diphenylamine as an indicator, no inside indicator was available in the titration of ferrous iron with an oxidizing agent. Since then other useful indicators have been found. A list of indicators with an oxidation potential higher than 0.70 volt with regard to the normal hydrogen electrode is given in Table I.

TABLE I. OXIDATION POTENTIALS OF INDICATORS

Indicator System	Oxidation Potential	Reduced form	Color Oxidized form
Ferrous nitrophenanthroline-ferrie nitrophenanthroline	1.25 (1 N H ₂ SO ₄)	Red	Light blue
Ferrous phenanthroline-ferrie phenanthroline	1.14 (1 N H ₂ SO ₄)	Red	Light blue
Porphyrexid-porphyrine	0.97 (pH = 7) 1.34 (pH = 0)	Red	Colorless
Porphyridine-leucoporphyrindine	0.81 (pH = 7) 1.2 (pH = 0)	Blue	Colorless
p-Nitrodiphenylamine-p-nitrodiphenyl violet	1.06 (1 N H ₂ SO ₄)	Colorless	Violet
Diphenylbenzidine sulfonic acid-diphenyl violet	0.87 ± 0.1	Colorless	Violet
Diphenylbenzidine-diphenylbenzidine violet	0.76 ± 0.1	Colorless	Violet
2,4-Diamino diphenylamine-2,4-diamino violet	0.70 (1 N H ₂ SO ₄)	Colorless	Red
Acetylamine diphenylamine-acetylamine violet	0.69	Colorless	Green-blue

The systems porphyrexid-porphyrine and porphyridine-leucoporphyrindine have been studied recently by Kuhn and Franke (5), but their indicator properties in titrations have not yet been investigated. The indicators belonging to the diphenylamine series (diphenylamine, diphenylbenzidine, diphenylamine sulfonic acid, diphenylbenzidine sulfonic acid) give brilliant color changes from colorless to violet. Especially the more soluble sulfonic acids have proved to be superior to the unsulfonated weak bases. The oxidized forms of these indicators have a limited stability and are subject to an irreversible oxidation, especially in the presence of a strong oxidizing agent. The triphenyl methane dyes of Knop (3), such as erioglaucin and eriogreen, are worse in this respect and for this reason are not listed. This irreversible reaction has to be taken into account in the titration of strong oxidizing agents, using indicators of the diphenylbenzidine series to detect the end point. In this respect the ferrous-ferrie phenanthroline system introduced by Walden, Hammett, and Chapman (9) is far superior to the diphenylbenzidine indicators. However, it should be realized that ferrous phenanthroline cannot be considered as a substitute for the diphenylbenzidine indicators, since the oxidation potential of the former is 0.3 to 0.4 volt higher than that of the latter. Evidently, there is still a need for indicators with oxidation potentials between about 0.7 and 1.1 volts. These may be found either by making a systematic study of various organic compounds, or by investigating the effect of the introduction of various groups in the existing indicators. Hosmer Stone has taken up a study of the properties of semidines and benzidines and their homologs and has found some useful indicators on which he will report in the near future. As far as the introduction of various groups is concerned, it may be expected that this will result in a change of the oxidation potential and of the stability of the oxidized form. Hammett, Walden, and Edmonds (2), for example, found that the introduction of a nitro group in diphenylamine raised the potential by 0.3 volt, although the oxidized form of this nitro indicator was found to be highly unstable.

Adsorption Indicators

Recently (4) a review of the properties of adsorption indicators has been given. From present experience one would conclude that the best analytical results are obtained with silver halide precipitates, and with mercurous chloride and bromide. Other precipitates seem to be less suitable, apparently because they exert less deforming effect upon the adsorbed dyes than the precipitates just mentioned. Adsorption indicators have been described in the literature for the titration of lead with chromate, sulfate, molybdate, and ferrocyanide, and of phosphate with lead (10), but these methods are of minor importance. More promising is a search for indicators suitable for the titration of chloride in relatively strongly acid medium. Acid dyes, the silver salts of which are slightly soluble and strongly colored, and which behave as strong acids, may be expected to be useful. The introduction of a strongly acid group, such as the sulfonic acid group, into an adsorption indicator, such as fluorescein, does not lead to the desired end, since even in the presence of the strong acid group the highly colored silver compound is the salt of a weak acid. On the other hand, the introduction of groups which results in an increase of the ionization constant of the common adsorption indicators—for example, of fluorescein—such as chlorine or nitro groups, extends the applicability of the indicators into a more strongly acid medium. It is for this reason that dichlorofluorescein has advantages over fluorescein.

Specific Indicators

If specific reagents were available which would form colored compounds instantaneously with various cations and anions, the number of titration methods might be extended almost indefinitely. The following indicators introduced recently in volumetric work may be quoted as examples:

Diphenylcarbazone for the titration of chloride or bromide with silver (1).

Tetrahydroxyquinone as indicator for barium in the titration of sulfate (6).

Zirconium alizarinate in the titration of fluoride.

α -Naphthoflavone as a reversible indicator for bromine in titrations with bromate (7, 8).

The systematic search for organic reagents specific for inorganic cations and anions, as originated by F. Feigl, undoubtedly will yield results of direct importance for volumetric analysis.

Summary

Possibilities for the further development of acid-base indicators for the measurement of hydrogen-ion activity and concentration, of oxidation-reduction indicators at high and low oxidation potentials, of adsorption indicators, and of specific indicators for volumetric purposes have been discussed.

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Spectrographic Microdetermination of Zinc

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THE recent development of interest in zinc as a necessary minor element in plant growth creates a demand for an analytical method capable of determining the minute quantities of this element that are present in vegetable matter. That the methods of spectrography are applicable to the determination of small quantities of zinc has been demonstrated by Rogers (3).

In the method proposed by Rogers, the ash of the plant material is arched directly, after incorporation of the "reference element." Since there is a limit both to the amount of ash that can be arched conveniently and also to the spectrographic sensitivity for zinc, his method has a limited usefulness. Rogers places the lower limit at about 0.002 per cent or 20 parts per million in the plant ash. Inasmuch as the concave grating spectrograph used by the authors is not so sensitive as the quartz prism instruments,¹ the zinc present in the plant ash must be separated from the main constituents of the ash and concentrated before spectrographic methods can be applied.

Experimental

In brief, the method proposed by the authors consists of dissolving the plant ash in dilute hydrochloric acid, adding 2 mg. of cadmium as the sulfate, precipitating the cadmium and zinc with hydrogen sulfide at a pH of about 3, and estimating the zinc in the sulfide precipitate spectrographically. The added cadmium is used as the "internal standard."

SEPARATION OF THE ZINC. A sample of from 2 to 4 grams of the dried plant material contained in a sillimanite combustion boat (100 mm. long and 20 mm. wide) is thoroughly ashed at a temperature of 450° C. in an electrically heated Pyrex-tube combustion furnace. The ash is transferred to a small evaporating dish, 20 ml. of *N* hydrochloric acid solution being added; the dish and contents are heated on a hot plate until the volume of the solution is reduced one-half. The solution is then filtered, the volume of filtrate and water washings being kept down to about 25 ml. To the filtrate, contained in a 125-ml. Pyrex Erlenmeyer flask, are added 10 ml. of cadmium sulfate solution containing 0.2 mg. of cadmium per ml. In the precipitation of zinc and cadmium sulfides, a modification of the technic of Fales and Ware (1) is used. With bromophenol blue as indicator the solution is adjusted to a pH of about 3.6 with saturated potassium hydroxide solution; 0.5 ml. of 50 per cent formic acid (sp. gr. 1.2) and 3 to 5 ml. of citric acid-sodium citrate buffer solution

are added. This buffer solution contains about 120 grams of sodium citrate ($2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$) and 230 grams of citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) per liter and is adjusted to a pH of 3.0.

The final volume of the solution should be about 40 ml. and the pH about 2.8 to 3.0. The contents of the flask are heated to about 60° to 70° C. and the flask is stoppered with a cork containing the hydrogen sulfide inlet tube and an outlet tube. The former extends nearly to the surface of the solution. A slow stream of hydrogen sulfide is passed into the flask as it is being heated. When the contents of the flask have reached the boiling point, the source of heat is removed and the outlet tube is closed. However, the flask is left connected to the hydrogen sulfide generator until it has cooled to room temperature. The flask is shaken occasionally during the cooling period. When cool, the flask is disconnected from the source of hydrogen sulfide, stoppered, and allowed to stand for about half an hour.

The contents of the flask are transferred to a 50-ml. Pyrex centrifuge tube; the flask is rinsed once with a few milliliters of 0.05 *N* formic acid solution saturated with hydrogen sulfide. After the centrifuging, the supernatant liquid is poured off and the precipitate in the tube is washed once with about 10 to 15 ml. of the hydrogen sulfide-formic acid solution. After a second centrifuging, the wash solution is poured off. The precipitate in the tube is dried overnight in an evacuated calcium chloride desiccator.

The washing of the precipitate and the drying at room temperature are absolutely essential, since only by so doing can one obtain a loose powdery precipitate which can easily and almost completely be transferred to the crater of the graphite electrode. The dried precipitate in the tube is loosened by means of a small platinum spatula and is transferred as completely as possible to the crater of the electrode. The electrodes used in these experiments were of graphite 0.64 cm. (0.25 inch) in diameter, with the crater 0.32 cm. (0.125 inch) both in diameter and depth.

SPECTROGRAPHIC EQUIPMENT. The spectrograph (Figure 1) used in this work is a concave grating instrument (made by the Applied Research Laboratories of Los Angeles).

The grating, whose radius of curvature is 150 cm., is ruled for a space of 5.1 cm. (2 inches) with lines 2.54 cm. (1 inch) long; it has approximately 9200 lines per cm. and consequently has a resolving power several times that of the large quartz prism spectrographs. The grating is ruled on speculum metal and is aluminized in vacuum after being ruled; by this means the reflective power is greatly increased, especially in the ultraviolet region. The arc is entirely enclosed, its image being focused on the grating by means of a quartz lens. The camera uses standard 35-mm. negative motion picture film. The ultraviolet region from 2370 Å. to 4600 Å. is photographed on a film 32 cm. long with the slit in one position. A second slit position is provided for photographing the visible spectrum from 4580 Å. to 6810 Å. on a film 32 cm. long; a disk of Crookes No. 1 glass placed in front of the slit absorbs the second order ultraviolet when the visible region is being photographed.

Owing to the astigmatic properties of the concave grating, it is difficult to use the revolving logarithmic sector of Scheibe and Neuhäusser (4). This difficulty has been overcome by Hasler and Lindhurst (2) by the introduction of a half-cylindrical shutter immediately in front of the photographic film. This shutter has its axis of rotation at the center of the cylinder and is so mounted that this axis is parallel to the plane of the film and normal to the plane of the light beams forming the spectral lines. The theory of such a shutter is given in the paper of Hasler and Lindhurst (2). The type of spectrograms obtained with such a revolving sector is shown in Figure 2, in which picture there are two such spectra with an iron comparison spectrum between them. The distance between the points at which a spectrum line fades out, *L*, is measured with a scale mounted in the eyepiece of the comparator microscope. The theory of such a shutter leads to the following simplified expression:

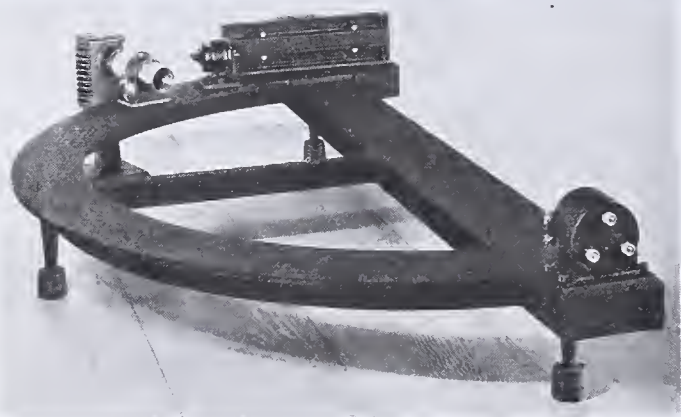


FIGURE 1. CONCAVE GRATING SPECTROGRAPH

¹ The speed of this grating spectrograph is somewhat less than that of the usual quartz prism instruments because of the fact that it was designed to give much higher resolution and dispersion in the visible region than most prism instruments possess.

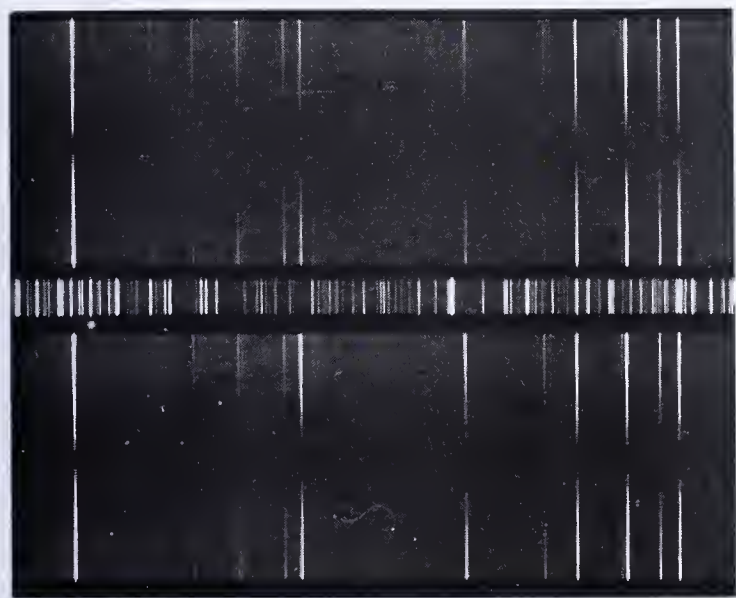


FIGURE 2. SPECTROGRAMS OBTAINED WITH HALF-CYLINDRICAL SHUTTER

$$L_1/L_2 = I_2/I_1$$

in which L_1 and L_2 are the lengths of the blank spaces between the points at which the two lines fade out, and I_1 and I_2 are the intensities of the two lines being compared.

CALIBRATION OF THE SECTOR. For the spectrographic estimation of zinc, the "internal standard" method was used. Cadmium was chosen as the internal standard for several reasons: (1) The cadmium line at 3252.5 Å. is of the same type as the zinc line at 3345.0 Å., is conveniently situated, and is of approximately the right intensity when 2 mg. of cadmium are co-precipitated with the zinc. (2) The volatilities of cadmium sulfide and zinc sulfide are sufficiently similar so that the two elements are vaporized at the same time; this is a rather important point since the "wandering" of the arc is a possible source of serious error if the two elements are not vaporized simultaneously. (3) Cadmium does not occur in plant materials in amounts sufficient to augment appreciably the 2 mg. added as internal standard.

Mixtures with known ratios of cadmium sulfide and zinc sulfide were made up. Placed in the cavity of a graphite electrode, 2.5 mg. of each of these dry powders are arched as the lower and positive electrode with a direct current of 7 amperes and 150 volts. Twenty seconds are sufficient to vaporize the sulfides completely, but all exposures were made for one minute. A slit width of 0.05 mm. was used, and the sector revolved at about 500 r. p. m.

The results of the spectrograms of these ratio powders are shown graphically in Figure 3. The zinc line at 3345.0 Å. is compared with the cadmium line at 3252.5 Å., and in the figure the ratio LCd/LZn is plotted against the square root of the number of milligrams of zinc present for each 2 mg. of cadmium.

TABLE I. EFFECT OF CURRENT ON RATIO OF INTENSITIES OF CADMIUM 3252.5 AND ZINC 3345.0 LINES	
Current, Amperes	LCd/LZn
4 to 5	1.25
4 to 5	1.27
7 to 8	1.30
7 to 8	1.28
11 to 12	1.25
11 to 12	1.27

The data in Table I strongly indicate that the pair of lines used in this investigation are invariant. In each case, 2 mg. of cadmium and 0.1 mg. of zinc as the sulfides were used.

ESTIMATION OF ZINC IN PURE SOLUTIONS. Solutions containing 2 mg. of cadmium as the sulfate and varying amounts of zinc as the sulfate were precipitated, washed, dried, and arched in the manner described in this paper. The spectrograms were measured, and from the values of the ratio LCd/LZn the recovery of zinc was obtained from the curve of Figure 3. The results are presented in Table II.

TABLE II. SPECTROGRAPHIC ESTIMATION OF ZINC RECOVERED FROM PURE SOLUTIONS

Zinc Taken Mg.	Zinc Found Mg.
0.01	0.010 and 0.012
0.025	0.023 and 0.022
0.05	0.057 and 0.048
0.075	0.078 and 0.078
0.10	0.090 and 0.108
0.20	0.185 and ...

RECOVERY OF ZINC ADDED TO PLANT TISSUE. Varying amounts of zinc as the sulfate were added to the ash resulting from the ignition of 2 grams of dried orange leaves (No. 358). Similar amounts of zinc were added to 2 grams of the leaf tissue (No. 358) before ignition. The results of these experiments are given in Table III.

TABLE III. RECOVERY OF ZINC ADDED TO PLANT TISSUE BEFORE AND AFTER IGNITION

Zinc Added Mg.	Recovery of Zinc Added before Ignition		Recovery of Zinc Added after Ignition	
	Mg.	Mg.	Mg.	Mg.
None	0.006	0.010		
0.05	0.058	0.062	0.057	0.048
0.10	0.096	0.108	0.108	0.096
0.15	0.152		0.144	0.152
0.20	0.193	0.176	0.212	0.203

As shown by these data, the recovery of zinc added to the plant tissue before ignition is quite satisfactory. Only in the case of the highest amount of zinc used (0.2 mg.) is there any indication of a loss due to ignition, and these few determinations can scarcely be considered conclusive.

TABLE IV. ZINC CONTENT OF CITRUS LEAVES
(Parts per million on air-dried basis)

Sample No.	Zinc P. p. m.
346	2.0
358	3.0
356	8.0
370	12.5
374	20
379	27
368	30
294	85

In Table IV are shown a few typical results of the analyses of citrus leaves. The zinc content is expressed as parts per million on an air-dried basis.

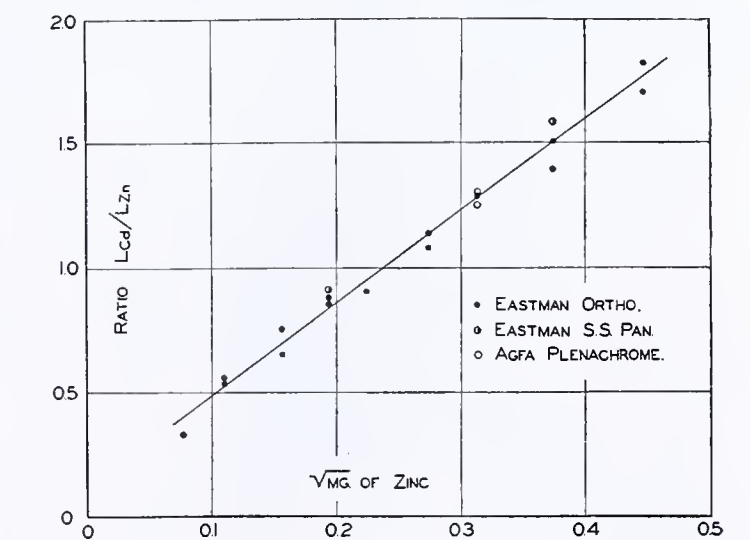


FIGURE 3. CALIBRATION CURVE

The data presented in Tables II and III show that the error is usually about 10 per cent but occasionally amounts to 20 per cent. It may be possible to reduce the error by using a photoelectric comparator for evaluating the relative intensities of the lines; the authors have not tried this.

Limits of the Method

The upper limit of this method is probably somewhat higher than 0.2 mg. of zinc; the authors made no attempt to ascertain the upper limit, since it is unlikely that amounts larger than 0.2 mg. of zinc would be encountered in 2 grams of plant tissue. If such were the case, one could use a smaller sample. The lower limit of the method, with the concave grating, is about 0.005 mg. of zinc, which on a 4-gram sample amounts to about 1 part per million. With a quartz prism spectrograph, both the upper and lower limits may be considerably lower.

Interference

This proposed method of precipitating the zinc as the sulfide along with the reference element, cadmium, also includes in the precipitate all the other elements whose sulfides are insoluble in a weakly acid solution. However, none of these other elements occur in plant tissue in amounts sufficient

to interfere in any way with the spectrographic determination. Moreover, the single sulfide precipitation and the single spectrogram would suffice for the determination of many of these other elements, provided that the calibration curve had been constructed for each of them.

Summary

A quantitative spectrographic method for the determination of zinc in plant material has been studied and presented. The range of the method is from about 1 to 100 p. p. m., or more, depending on the size of the sample used. Cadmium is used as the internal standard, the zinc and cadmium being co-precipitated as the sulfides before arcking. No other elements are present in the sulfide precipitate in amounts sufficient to cause interference. The maximum deviation from the mean of duplicate analysis is about one part in five.

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Photometric Determination of Iron in Used Engine Oils

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The iron content in the ash of oils subjected to service tests may be readily determined by means of a photometric colorimeter. Even small amounts of wear may be followed closely without interfering with the continuous operation of the motor.

SMALL amounts of iron are frequently determined through the formation of ferric sulfocyanide, visual matching with the color produced in a sample containing a known amount of iron being utilized. The proposed method involves measurement of the intensity of color produced by means of light from a fixed source passing through a thin layer of solution in which ferric sulfocyanide has been formed, and impinging upon a photronic cell. This has been applied especially to the determination of iron in used crankcase oils.

It is well known that internal-combustion engine wear may be estimated from the iron content of the crankcase oil (1, 3, 4, 5). Such a means of attack on this important problem carries with it several advantages over wear determination by micrometer measurement or by change in weight of certain parts during a run. It is not necessarily true that all parts of the engine are abraded to the same extent as those measured or weighed. A long engine test with its attending expense and inconvenience is needed to obtain the desired accuracy of measurement; under these circumstances conditions in the motor may vary to such an extent that a fair comparison of two oils in successive runs may not be secured. The lubricating oil, however, reaches all parts of the motor

subject to wear—it is reasonable to suppose that its total iron content is an index of the abrasion which has occurred.

Very small amounts of wear, undetectable by physical measurement, may be estimated. About 10,000 miles of engine operation are required to cause cylinder wear of 0.0025 cm. (0.001 inch), while the wear in 10 miles may readily be detected by this chemical method. Furthermore, the progress of wear may be followed without even stopping the engine.

The method permits one man to make six iron determinations in duplicate in 8 hours, and is applicable to the determination of iron in amounts from 0.00005 to 0.0015 gram. Duplicate runs on each of 321 used oils showed an average difference of 3.8 per cent. It is considered that this difference is due largely to difficulty in sampling, as the average difference encountered with calibration samples containing known

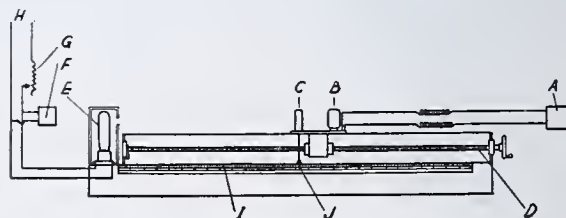


FIGURE 1. PHOTOMETRIC COLORIMETER

- A. Direct current microammeter
- B. Weston photronic cell, Model 594
- C. Glass cell for solution
- D. Screw arrangement for moving cells
- E. Light source (100-watt 115-volt Mazda lamp)
- F. Alternating current voltmeter
- G. Voltage control rheostat
- H. Alternating current source
- I. Meter stick
- J. Indicator pointer

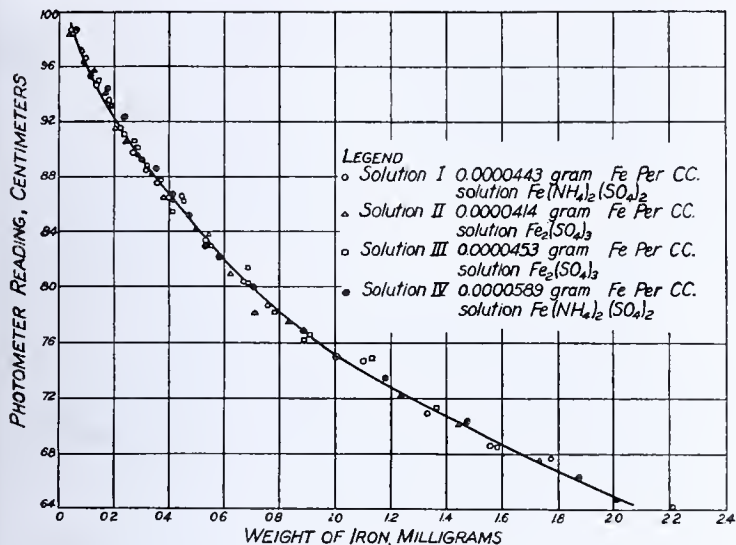


FIGURE 2. CALIBRATION CURVE OF PHOTOMETER FOR IRON ANALYSIS

amounts of iron was 0.4 per cent. Runs on oils to which ferric oleate had been added gave an average result 0.2 per cent higher than the theoretical amount, the greatest deviation for any one of the four samples being 3.58 per cent. These data are shown in Table I. The colorimetric analysis of the oleate itself is indicated in Table II.

TABLE I. ANALYSES OF OILS CONTAINING FERRIC OLEATE		
Iron Present %	Iron Found %	Difference %
0.000446	0.000455	+2.02
0.000446	0.000462	+3.58
0.000446	0.000436	-2.24
0.000446	0.000436	-2.24
Av. 0.000446	0.000447	+0.2

TABLE II. COLORIMETRIC ANALYSIS OF FERRIC OLEATE		
Sample Gram	Iron Present %	Iron Found %
0.0990	6.21	6.3
0.0990	6.21	6.2
0.0333	6.21	6.0

In the determination of iron by the sulfocyanide method, silver, mercuric chloride (6), cobalt (8), and bismuth (2) should be absent. It is stated that tests are best carried out in the absence of phosphates, borates, oxalates, acetates, tartrates, and citrates (7). Oxalic and phosphorous acids interfere (10); the color produced by nitric acid is destroyed on boiling, though it might be mistaken for that of iron in the cold. Alkaline earth chlorides are detrimental (8). Organic matter, certain mineral acids, and many metals do not cause any difficulty.

Experimental

The procedure consists in general of ashing the oil, dissolving the residue in hydrochloric acid, adding ammonium sulfocyanide solution, and estimating the amount of iron present from the intensity of light projected by a fixed source through a thin layer of solution upon a photronic cell. The instrument, shown in Figure 1, in which color comparison was made was a colorimeter similar to that of Story and Kalichevsky (9), and consisted essentially of a fixed light source and a movable photronic cell with a container between them for the sample. The last two items were mounted on a movable carriage which was so placed in operation as to produce a certain specified current from the photronic cell. It

is obvious that calibration may be effected by using samples of known iron content and noting the distance of a mark on the movable carriage from the light source. It was thus not necessary to have constantly on hand standard solutions for comparison. Color matching by visual inspection may introduce large personal error or may even be impossible for some operators. The current from the photronic cell, however, was read on a microammeter and could be adjusted to the desired value very readily.

STANDARDIZATION OF PHOTOMETER. A glass cell, 50 × 50 × 10 mm., filled with distilled water was placed in a holder directly in front of the photronic cell. With an indicator on the movable platform 100 cm. from the light source, the intensity of the latter was adjusted by varying the current until a microammeter showed the photronic cell to be delivering 19 microamperes. This value was arbitrarily chosen as a convenient one for use. The standardization of the colorimeter was effected by the use of solutions of ferric iron. Solutions containing up to 0.0022 gram of ferric iron were prepared by well-known procedures from ferrous ammonium sulfate and ferric sulfate which had been analyzed gravimetrically for iron content. To 90 cc. of solution containing the desired amount of iron 10 cc. of *N* ammonium sulfocyanide were added (this is equivalent to at least twenty-five times the maximum amount, 0.0015 gram, of iron present). The mixture was placed in the glass cell directly in front of the photronic cell, and with the light source maintained at the voltage determined by the use of distilled water at 100 cm., the position of the assembly was varied until the current from the photronic cell became 19 microamperes. The calibration curve as shown in Figure 2 was obtained in this way. It was found that the iron present in reagents (iron-free hydrochloric acid and ammonium thiocyanate) was so small that no correction was required. **PROCEDURE.** A 10-gram representative sample of the oil was very carefully ashed in a quartz crucible. No fusion of the ash with the quartz crucible was noted; however, platinum may be used if desired. To the ash in the cooled crucible were added 20 cc. of iron-free, concentrated hydrochloric acid with gentle heating to dissolve any oxide sticking on the walls. The mixture was then washed into a beaker and boiled for 10 minutes. The liquor was transferred to a 100-cc. graduated cylinder and diluted to 90 cc. Next 10 cc. of normal ammonium sulfocyanide were added with thorough mixing. A portion of the mixed solution was put in the glass cell, the voltage of the light source was adjusted to the value used in calibration, and the position of the carriage holding the glass cell and photronic cell fixed to give a current of 19 microamperes. The amount of iron in the sample was then found from the calibration curve. Should there be any turbidity or evidence of suspended material in the colored solution, it must be filtered before being introduced into the containing cell.

Discussion of Results

This method has been found to be suitable for the estimation of iron in amounts ranging from 0.00005 to 0.0015 gram. Aliquot portions of solutions containing large amounts of iron may be taken for analysis. With amounts of iron in the cell greater than about 0.0015 gram, the reproducibility of the method does not justify its use.

The results shown in Figure 3 may be taken as illustrative

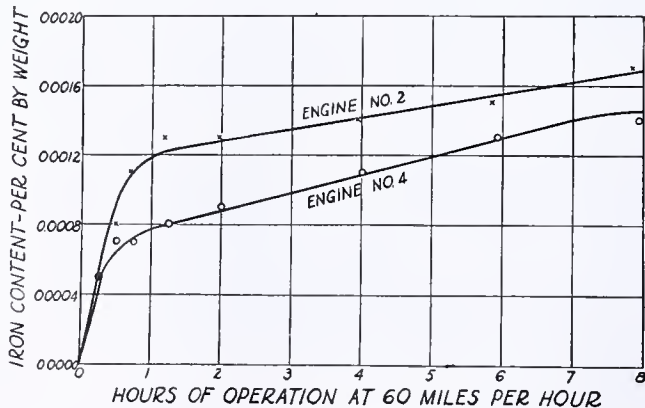


FIGURE 3. WEAR IN TWO DODGE ENGINES LUBRICATED WITH THE SAME OIL

of the increase in iron content of an oil in engine service. No correction has been made for the oil consumed during the run. The same oil and operating conditions were used, but different engines were involved in the two cases shown. The rapid increase in iron content at the beginning of a run is of interest. It has long been known that intermittent service causes greater engine wear than continuous running. The colorimetric method of analysis for iron is a convenient means of confirming this circumstance and affords an indication of rates of wear under various conditions.

Acknowledgment

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Identification of Crystalline Materials

Classification and Use of X-Ray Diffraction Patterns

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IN THE course of the past few years, x-ray and spectroscopic methods of analysis have found an increasing usefulness at the Dow Chemical Company. There are a large number of different types of problems on which information can be obtained by the variations of apparatus and technic which are possible in these two fields. It is not the purpose of this paper, however, to discuss these methods or applications in general, but to describe in some detail a scheme of classifying and using x-ray diffraction patterns which has been found very helpful in one particular application of x-rays—namely, that of identifying unknown substances by means of their Hull powder diffraction patterns.

The inherent power of x-ray diffraction as a practical means of chemical analysis was pointed out a good many years ago (2, 4). Having a different theoretical basis and depending upon an entirely different technic than other methods, it would be expected to supplement the information to be obtained from other methods and, at times, to be applicable where other methods are not suitable. It appears, however, that the use of this method has not increased at a rate commensurate with its unique and valuable features, and that it is used by relatively few academic and industrial laboratories.

Probably one of the main reasons for this is that x-ray diffraction is not a practical, economical method of analysis as long as it involves any time-consuming process such as the determination of crystal structure. For the purpose of analysis, however, there is no advantage in knowing the crystal structure, since any substance is just as uniquely characterized by its diffraction pattern. For practical usage, the x-ray diffraction method must be put upon an empirical basis, as has been done, for example, in spectroscopic analysis. There are available for the spectroscopist portfolios of the arc and spark spectra of the elements, and also convenient tables of wave lengths which serve to assist him in identifying

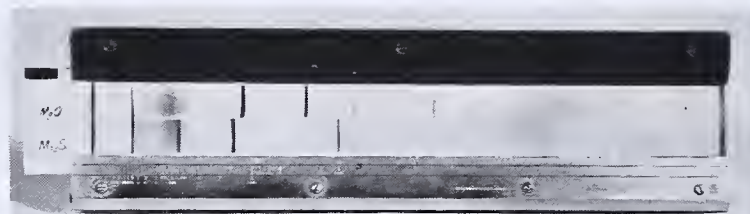


FIGURE 1. X-RAY POWDER DIFFRACTION PATTERNS IN CALIBRATED SCALE
MoK α radiation

the origin of the unknown lines in the spectra obtained.

Similarly, in the x-ray field, one of the things which will greatly facilitate the use of x-ray powder patterns in identifying unknowns is to have available a reference library of standard patterns of known substances. However, because

there are thousands of common chemical substances, the job of taking the standard patterns, and more especially of finding an adequate system of indexing or classifying thousands of diffraction patterns, is considerable and in general has not been thought feasible (6). It has been found in this laboratory that the problem of classification of the patterns presents no practical difficulties and that in so far as they can be obtained, they can be effectively used in the identification of unknowns. The real limitations to the field of applicability of the x-ray method are due to more fundamental factors, such as lack of sensitivity to small percentages of the minor constituent and to the small effects sometimes encountered in changes of solid solution concentration and lack of sensitivity because of the poor crystalline structure of some materials. A recent article by Waldo (5) gives the results of a similar attempt at classification applied to about 50 copper-ore minerals. A comparison of the classifications will be made in connection with the detailed description of the present method.

Identification of complete unknowns does not form the bulk of the work or the most important part of the application of x-ray diffraction patterns. However, as the stock of patterns obtained in the course of the authors' use of x-ray diffraction continued to enlarge, the advantage of having an index to them became apparent. The system of classification which was finally adopted has been in operation since June, 1934, and, though the number of patterns has greatly increased since that time, has proved to be fully adequate to handle them. The authors now have over 4000 patterns, of which 1054 are individual inorganic chemical substances.

These constitute a reference file which can be used in this field in much the same way that fingerprints are used to identify persons (?). This is not a large stock, but it is large enough to permit one to form a judgment of the capacity and practicability of any particular system of classification. This system of classification permits a pattern to be identified in a few minutes, even though it is a composite of individual patterns, provided these individual patterns are present in the reference file.

Method of Classification

Choosing a method of classification is merely a matter of investigating how many measurements of the pattern are necessary to distinguish it from other patterns. Theoretically, no two different substances could have exactly the same pattern. The powder pattern of a substance is made up of lines in certain positions and of certain intensities. The more of these parameters used, the more certain is the identification. One might choose to measure and record accurately and completely the positions and intensities of all the lines of the pattern, or to measure and record only enough data from the pattern to serve to locate it, and then check all details by comparing directly with the known file pattern (or a print of it). The first method would require a great deal of work in measuring the pattern and even then would be no improvement in accuracy over direct comparison by eye. The second method is practicable because, as investigation has shown, three easy measurements are sufficient to give the approximate location of the pattern in the file, and one can then visually check the entire pattern without ever having to make difficult measurements.

The powder patterns are produced using molybdenum radiation and the General Electric diffraction unit. Figure 1 shows two such patterns placed in the calibrated scale which gives, in Ångström units, the interplanar distances of the crystal planes giving rise to the diffracted lines. The Å. positions of the three strongest lines of the diffracted pattern are read off in the order of decreasing intensity. However, for purposes of classification, the lines are listed only according to the particular divisions of the scale in which they fall. The sizes of the divisions into which the classification book is arbitrarily divided are: 0.1 Å. divisions below 1.0 Å., 0.05 Å. divisions from 1.0 to 3.0 Å., 0.1 Å. divisions from 3.0 to 5.0 Å., 0.25 Å. divisions from 5.0 to 6.0 Å., and 0.5 Å. divisions from 6.0 to 8.0 Å. The size of these divisions is determined by the consideration that they can be no smaller than is consistent with the accuracy of measurement of the position of the lines, and that they should be no more numerous than is necessary

to handle conveniently all the patterns without conflict, thus minimizing the result of errors of measurement. Actually, the divisions chosen are 5 to 10 times the error of measurement. Using molybdenum radiation and a specimen-film distance of 20 cm. (8 inches), the error of measurement increases in a smooth curve from ± 0.001 Å. at 1.0 Å., through ± 0.01 Å. at 3.5 Å. to ± 0.06 Å. at 8.0 Å. In order to secure this accuracy, all cassettes used are calibrated against the sodium chloride and copper patterns.

It is not necessary to use a densitometer to measure densities of lines. If two lines appear to be so closely the same density that it is hard to decide by eye which is the more dense, the rule is to list the one of the greater Å. spacing first. One thus has, as a characteristic of each pattern, three numbers in a certain sequence. The patterns are then listed, at the proper place, in an indexed book which is divided and subdivided into the arbitrarily chosen regions as given above. The first number determines the group, the second number the subgroup, and the third number the location within the subgroup. Figure 2 shows a typical page within the book.

After listing 1054 patterns of common inorganic chemicals in the classification book in this way, it is found that 1 subgroup contains 7 patterns, 5 subgroups contain 5 patterns each, 9 contain 4 patterns each, 38 contain 3 patterns each, 150 contain 2 patterns each, 582 subgroups contain only a single pattern each, and 3836 subgroups are unoccupied. (Because two patterns fall in the same subgroup does not mean that they are identical with respect to their first two lines, since their positions within the divisions may be different, and their relative intensities probably will be different.) Thus among these 1054 patterns it is not necessary to measure more than the two strongest lines in order to limit the possibilities to a few patterns. Looking now at the coincidences of third lines within a subgroup, there are 11 subgroups in which 2 patterns have the same position (within twice the \pm error of measurement) of the third line, and 4 subgroups in which 3 patterns have the same third line. In seven of these cases, a measurement of the fourth line serves to distinguish the patterns (a column is included in the book for recording the fourth line). However, in practice, after a pattern has been located in the book, it is taken out of the file and compared directly in all its details. It is thus easy to see at a glance differences which otherwise could be established only by careful measurements. When this is done, for the conflicts still remaining, there are only three cases left in which the patterns are not immediately distinguishable from each other, and in these cases, if there were nothing easier to do, a more accurate determination of planar spacings by a different x-ray technic would be sufficient. Probably, however, some other information would be available to assist in separating these very occasional conflicts.

Taking into account the number of subgroups and the distributions of the lines as they occur in the type of pattern with which the authors have worked, they estimate that the classification book in its present form, making use of three lines as described, would easily handle many thousands of patterns. If, for instance, there were 20,000 patterns in the file, there would be a total of only several hundred cases in which one would have to compare his unknown with two patterns from the file, and not more than about twenty cases in which one would have to compare with more than three patterns.

Identification of Mixtures

The problem is complicated somewhat and the process of identification lengthened, if the unknown is a mixture of substances. However, any component of a mixture of substances can be identified with just as much certainty (in so far as enough lines are visible) as if it were an isolated material,

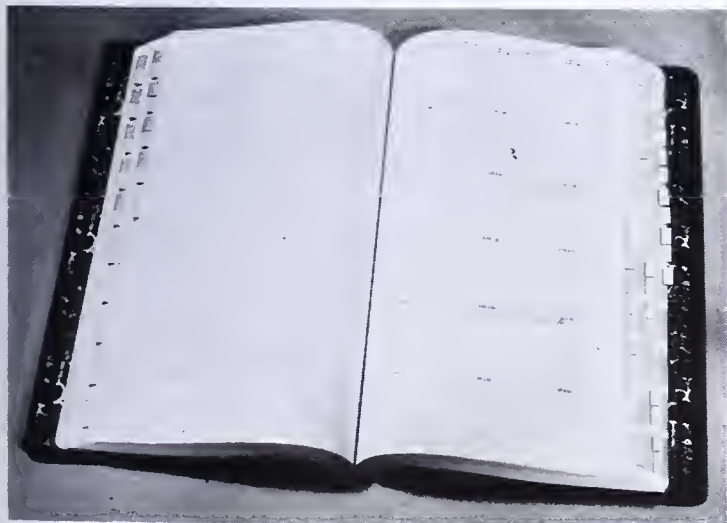


FIGURE 2. TYPICAL PAGE IN CLASSIFICATION BOOK

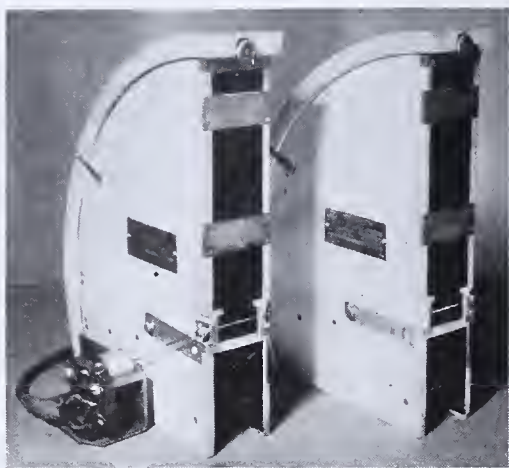


FIGURE 3. MECHANICAL AID TO ENSURE UNIFORM PATTERNS

provided its pattern is contained in the reference file. The procedure of identifying the unknown is the same whether the unknown pattern is a superposition of separate patterns or not.

To meet the possibility that the unknown is a mixture of patterns, it is necessary to read more than three lines, since the three strongest lines may include certain lines of each constituent. One begins with the strongest line, turns to the subgroup determined by the second strongest line, and sees whether any of the lines of the unknown check lines in this subgroup. (This can be done at a glance, since, of the subgroups which are occupied, the largest contains only seven patterns and most of them contain only one.) If the unknown is a single pattern, the third strongest line will check, and the pattern will have been located. If the second strongest line of the unknown pattern should happen to be the strongest line of a second component, the pattern would not have been found and one proceeds by using the third strongest line of the unknown pattern to determine the subgroup, and so on. When a match is found, the lines of the unknown coinciding with the standard are noted, as are also any intensity variations which would indicate superpositions of lines. The remaining unidentified lines of the unknown are then treated in the standard manner.

If the constituent corresponding to the strongest line of the unknown pattern is not contained in the file, one must proceed using the second strongest line to determine the main group, etc. One cannot fail to find any or all components of the mixture which exist in the reference file. The authors have numerous examples in which mixtures of three components were resolved and one case in which four components were present in an unknown and all identified. If the pattern cannot be found in the file, even in this case one has obtained considerable negative information about the unknown.

Other Classification Systems

It has been suggested (6) that, in a limited field, 100 or more patterns might be handled by listing, in the order of planar spacings, all the lines in all the patterns. This is closely analogous to the system commonly used in spectroscopy, in which the wave lengths of all lines are listed in order. This system would be practical for x-ray diffraction if planar spacings were accurately measured to four or five significant figures, but the authors' experience indicates that it is not practical when one measures to only 0.01 or 0.1 Å. When technic is developed to permit more precise measurements, it will be possible to multiply further the capacity of the classification book by choosing smaller sized divisions.

Waldo (5) has described a system of classification listing the exact positions of the lines in the order of their relative intensity, and this does not differ fundamentally from the system here under discussion. It would appear that there are practical advantages in the use of finite divisions and definite subgroups, in that addition of patterns to the file requires no rearranging of the patterns already on record, and, in looking up unknowns, the only possible location is definitely defined

except when the line falls on the boundary between divisions, in which case there are two possible locations. Also, as has been emphasized, the present system does not use the book for the final identification of the unknown but simply to locate the pattern in the file. This direct comparison is more accurate than measurements of positions and is particularly important for mixtures of patterns in which occasional superpositions of lines make careful comparisons of intensities desirable.

Weaknesses of X-Ray Diffraction Method

There are some definite limitations to the field of applicability of the x-ray method of analysis, but the important question is the range of usefulness left when these things are taken into account. One should have constantly in mind when using x-ray diffraction that it is valuable for what it does show, not for what it does not show. When a diffraction pattern is obtained, it is decisive evidence of the presence of the particular substance which gives rise to this pattern, but diffraction lines may be so weak that they are not detected and one must therefore be wary of drawing conclusions. There is always the possibility of the presence of amorphous phases. This is a definite weakness of the method and leaves one in the same position as the fingerprint expert who cannot find any fingerprints. The extent of this limitation of the x-ray method applied to inorganic solids is indicated by the fact that of 1000 substances taken at random from the chemical stockroom shelves, only 5 per cent are amorphous while 95 per cent are crystalline and have a characteristic pattern.

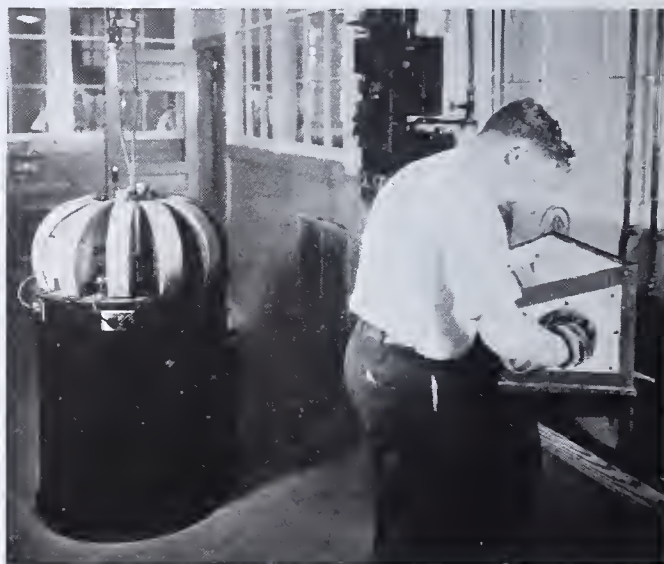


FIGURE 4. USE OF LOADING BOX FOR SUBSTANCES WHICH TAKE UP WATER IN AIR

The sensitivity of detection for the lesser constituent of a mixture is relatively low and will vary greatly from one substance to another, but in general will lie somewhere between concentrations of 0.1 and 10 per cent. For the determination of this figure, in any particular case, it is necessary to make up standard mixtures. Standard mixtures for comparison will also enable one to make semi-quantitative analyses throughout the whole range from 0 to 100 per cent. A development of this technic to the quantitative stage has been reported recently (1).

The type of pattern best adapted for general chemical identification—i. e., one with as many strong lines as possible—is not suited for the study of solid solutions in which it is necessary to measure lattice constants to a high degree of accuracy. Therefore, unless one has other information about the unknown, he may overlook the possibility that the pattern

of an unknown really represents a member of a solid solution series. The authors find that the combination of spectroscopy and x-ray diffraction is very fortunate, since they supplement each other's deficiencies by giving very different types of information about the same substance. In the arc or spark, the material is broken up into its elements so that they show regardless of the state in which they were present, while the x-ray without changing the material records the existing chemical and physical state. Thus for a complete unknown, the authors always supplement the x-ray diffraction with spectroscopic analysis or other information to check the possible presence of amorphous components or isomorphous systems.

Aids to Experimental Technic

Discussions of the theory and technic of x-ray diffraction can be found in many places (the most recent comprehensive book on the subject is by Davey, 3) and are outside the scope of this article. However, a few items of practical experience may be of interest.

To make full use of the x-ray, one should have the necessary equipment to adapt the type of camera and the source of x-rays to the particular requirements of the problem at hand. For general chemical identification, the authors find it most convenient to use molybdenum radiation. The greater penetration of the molybdenum radiation, as compared with copper or iron or other longer wave lengths, makes specimen mountings easier. The 16-hour exposures necessary with molybdenum radiation are not really a disadvantage, since the diffraction cameras can be loaded with as many as 24 specimens at night and the films are ready to develop in the morning. The batch processes of preparing specimens, developing films, etc., result in economy of time.

Figure 3 shows a simple mechanical attachment, readily installed on commercial cassettes, which ensures uniform patterns. At one end, the usual capillary tube passes through, and is fastened by wax to a metal pulley. The other end passes through a glass tube serving as a bearing. So many substances require rotation because of large crystals that the practical procedure is to rotate every specimen and avoid the necessity of repeating any of them.

Figure 4 shows a drier and loading box which is useful when handling substances which take up water. It is, for most materials, more convenient than the usual technic of loading under a protective liquid.

Summary and Conclusions

This investigation shows that, with the aid of a classification system as herein described, it is entirely practical to make effective use of a large library of standard x-ray diffraction patterns for the identification of unknowns, even when the unknown is a mixture of materials. This makes possible a more complete utilization of the unique features of the x-ray diffraction method of analysis. The unique features which have been found of practical importance in this laboratory are (1) the substances present show in their true state of chemical combination, especially useful for the study of reaction mixtures; (2) the analysis is very certain, even though only minute amounts of material are available; (3) substances are studied directly in their "as received" state and are not destroyed; (4) different crystalline phases, states of hydration, and physical state are observable, and (5) the process of preparing the specimen and obtaining the x-ray pattern is very simple. The fundamental limitations of the method lie in lack of sensitivity to small percentages of the minor constituents and in the noncrystalline nature of many substances.

While the present article is based mainly on the results obtained with inorganic substances, it is planned in the near future to investigate in a similar manner other fields, such as organic solids, intermetallic compounds, etc.

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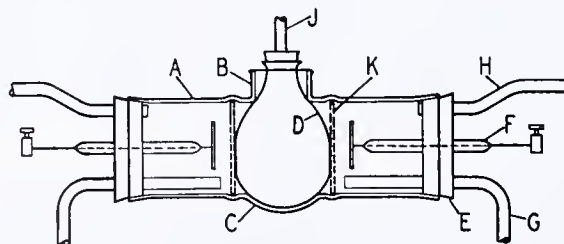
A Simple and Inexpensive Electrodialyzer

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A SIMPLE, inexpensive, and effective apparatus for electrodialysis can be made in almost any laboratory.

It consists of a glass tube, A, 6 cm. in diameter and 20 cm. in length, in which there is an opening formed by sealing in a short tube, B, about 5 cm. in diameter and 4 to 5 cm. in length. Each end of the large tube is closed tightly with No. 13 rubber stoppers through which three holes have been bored, one in the center in which is supported an electrode, F, and two others through which glass tube, G, for inflow of water, and glass tube, H, for outflow of water are inserted.

The dialyzing medium consists of a collodion sack, D, which is prepared in a round-bottomed flask, treated with water, removed and inserted through tube B into the dialyzer. (A suitable collodion for use in the preparation of dialyzers can be made up by adding to 3 grams of nitrocellulose 25 cc. of ethanol, allowing this mixture to stand for about 15 minutes, then adding 75 cc. of ether.) The liquid to be dialyzed is put into the sack. A tube 6 cm. in diameter will take a collodion sack made in a 200-cc. round-bottomed flask. If the tube is bulged slightly, as shown at C, it will take a sack made in a 500-cc. round-bottomed flask and the chamber will be more nearly the shape of the sack, so that a tighter fit of the sack will be obtained. Perforated disks (celluloid or pyralin), K, may be fixed in the tube by slightly



bulging it to hold them. These disks will act as supports to the collodion sack and will prevent the walls of the sack from coming in contact with the electrodes. An outlet tube, J, is inserted through a stopper in the neck of the sack to avoid building up high osmotic pressure within the sack.

The principal advantage of this apparatus consists in the ease with which the diaphragm membranes can be prepared and held in place. This makes the apparatus especially adaptable for student laboratory work.

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Nephelometric Determination of Fluorine

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IN THE analysis of rocks and minerals fluorine has long been regarded as a troublesome element. Although in rocks the determination of fluorine is frequently omitted, it is an essential constituent of many minerals. Phosphate rocks usually contain an appreciable quantity and it is found in some micas, particularly biotite, in hornblende, in tourmaline, and in certain fluorine minerals. Although not an abundant element, fluorine must be frequently determined in mineral analysis. Few methods of determining fluorine are available, and most of them are time-consuming.

The evolution method, whereby fluorine is distilled as silicon tetrafluoride, is described by Reynolds, Ross, and Jacob (10). The yield is stated by Hillebrand and Lundell (6) to be about 92 to 94 per cent of the fluorine, and a large correction factor is necessary.

Steiger's method (15), which consists in measuring the bleaching effect of fluorine on oxidized titanium solutions, is useful in the estimation of small percentages of fluorine in rocks but is not sufficiently accurate for the determination of large percentages.

The volumetric method of Knoblock (8) was improved by Fairchild (4), who reported some satisfactory results. The present writer, however, obtained discordant results with the method. It depends on the formation of un-ionized ferric fluoride when a standard solution of ferric chloride is added to the fluoride solution. The excess of ferric chloride sets free iodine from potassium iodide, and the iodine is determined by titration.

Minute quantities of fluorine in natural waters may be determined by the colorimetric method of Foster (5), which depends on the bleaching of ferric thiocyanate by fluorine solutions. Other methods for determining fluorine in water are described by Armstrong (1), Wilcox (18), Thompson and Taylor (16), Sanchis (11), and Barr and Thorogood (2).

Accurate results are reported by Hoffman and Lundell (7) by the use of a modification of the lead chlorofluoride method, originated by Starck (13). The compound, $PbClF$, is precipitated and weighed as such or the chlorine is determined by the Volhard method. The method is not satisfactory for the analysis of phosphate rock or in the presence of much phosphoric acid.

An older method, still much used, is the gravimetric method of Berzelius (3), consisting of precipitating and weighing the fluorine as calcium fluoride. If precipitated alone, calcium fluoride forms a fine suspension which cannot be readily filtered. It is therefore precipitated together with calcium carbonate, filtered, ignited, and weighed, after which the calcium carbonate is removed by several treatments with dilute acetic acid and the purified calcium fluoride is again ignited and weighed. The precipitate may be contaminated by sulfates, phosphates, and chromates. Precipitation of calcium fluoride in conjunction with the oxalate is described by Starck and Thorin (14).

The tendency of calcium fluoride to precipitate as a fine suspension suggested the possibility that the precipitate might be measured nephelometrically. Preliminary results, although promising, showed the need of reducing the solubility by adding alcohol and of stabilizing the suspension with a protective colloid. Gelatin was found satisfactory as a protective colloid, keeping the calcium fluoride in colloidal suspension almost indefinitely.

The procedure finally developed gives results which appear to be accurate to about 1 per cent of the fluorine. For samples requiring a carbonate fusion the lower limit of the method is about 0.3 per cent of fluorine, although for water-soluble materials, such as salines, a smaller percentage may be determined.

Fluorine in minerals may be determined with the nephelometer to about 1 per cent of the fluorine. The determination is made on an aliquot of the sodium chloride solution of the fluorine, obtained by the Berzelius method of extraction. The fluorine is precipitated as colloidal calcium fluoride in alcoholic solution, gelatin serving as a protective colloid. Arsenates, sulfates, and phosphates, which interfere with the determination, must be removed.

Preliminary Separation of Fluorine

The preliminary decomposition and removal of silica, alumina, etc., is effected by the Berzelius method, essentially the procedure given by Washington (17). Hydrochloric acid is used throughout the procedure instead of nitric acid.

About 2 grams of powdered mineral (or a smaller quantity if the fluoride content is high) are fused with 10 grams of anhy-

drous sodium carbonate until decomposition is complete. The cake is thoroughly leached with hot water, filtered, and washed. If there is any reason to doubt the completeness of the extraction, the residue and paper are ignited at a low heat and fused with 2.5 grains of sodium carbonate, the cake is extracted as before, and the second extract added to the first.

To the combined filtrates, containing the fluorine, about 3 grams of powdered ammonium carbonate are added. The solution is digested for 1 hour at 40° C., allowed to cool, and 1.5 grams more of ammonium carbonate are added. After standing 12 hours the solution is filtered, and the beaker and precipitate are washed with weak ammonium carbonate solution. The filtrate is boiled until the odor of ammonia can no longer be detected. The burner is removed, a few drops of methyl red are added, and then hydrochloric acid is added until the red color appears. If phosphates are present 1 ml. of 0.1 *N* ferric chloride is added, and then weak sodium hydroxide until the iron is precipitated and the methyl red just becomes yellow. About 0.5 gram of 20-mesh metallic zinc in the solution removes arsenic and prevents bumping when the solution is boiled. Two milliliters of a strong solution of zinc oxide in ammonium carbonate solution containing ammonia are added, and the solution is boiled (covered) until free from ammonia and then filtered and washed with water.

Most of the determinations on minerals, described later, were made using the above procedure for removing silica. Double precipitation with zinc oxide, as recommended by Hoffman and Lundell (7), requires less time and was later adopted.

If sulfates or chromates are present in appreciable quantity they are removed by adding barium chloride, avoiding an excess. The small quantities of sulfates usually present in silicates may be ignored.

The solution, in a platinum dish, is evaporated on the steam bath to about 100 ml., cooled, and filtered into a volumetric flask of volume such that the concentration of sodium chloride will be 55 grams per liter. Thus, if 10 grams of sodium carbonate were used in the extraction of fluorine, a 200-ml. volumetric flask is used.

The filtrate is made just acid to methyl red with weak hydrochloric acid, then just alkaline with weak sodium hydroxide, diluted to the mark, and thoroughly shaken.

Nephelometric Measurement of Fluorine

REAGENTS. Two grams of gelatin in 40 ml. of distilled water are heated on the steam bath with occasional shaking until dissolved to make the 5 per cent gelatin solution. If the solution congeals on cooling, it is warmed slightly until fluid. A fresh solution should be made every few days.

The precipitant is prepared by making 100 ml. of a solution containing 20 grams of calcium chloride just acid to methyl red with 0.1 *N* hydrochloric acid and adding 2 ml. excess of 0.1 *N* hydrochloric acid. This solution is diluted with 100 ml. of distilled water and filtered through an S. & S. 589 or Whatman No. 42 paper.

Commercial 95 per cent alcohol.

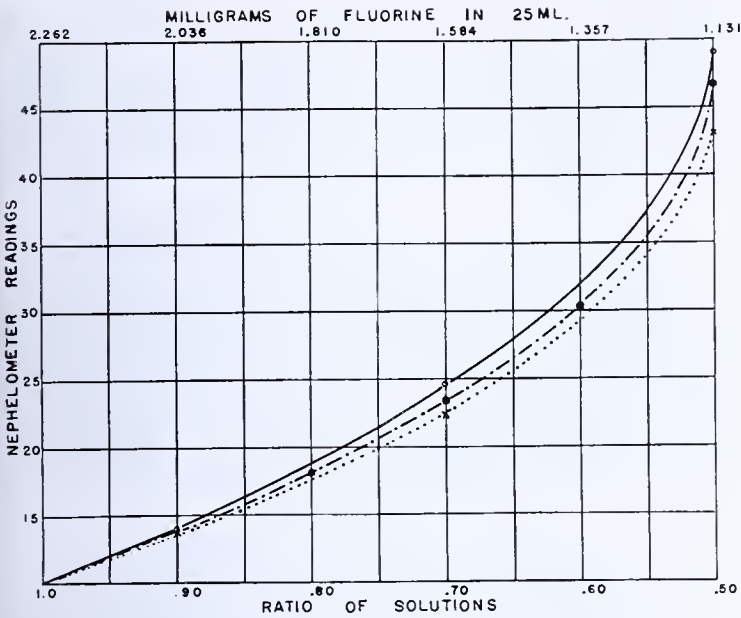


FIGURE 1. NEPHELOMETRIC CURVES OBTAINED ON DIFFERENT DAYS

Sodium chloride solution, 55 grams per liter, filtered through a fine paper.

To make the standard sodium fluoride solution, c. p. sodium fluoride is dissolved in water, filtered, and twice recrystallized. The pure crystals are dried, crushed, then heated for 2 hours at 500° C. The pure sodium fluoride is kept in a wide-mouth glass-stoppered bottle, the stopper being coated with petrolatum to exclude moisture. Of this 0.2000 gram is weighed accurately and made up to 1 liter with the sodium chloride solution (55 grams per liter). The flask is shaken until solution is complete; then the standard is stored in a bottle coated inside with paraffin.

APPARATUS. The nephelometer used was a Bausch & Lomb Kober constant upper-end type, with nephelometer cups of 5-ml. capacity and lamp-housing equipment.

Volumetric flasks and pipets of different capacities.

PROCEDURE. A 25-ml. aliquot of the unknown solution is taken with a pipet and placed in a wide-mouth glass-stoppered bottle. A number of other unknown solutions may be determined at the same time. Twenty-five milliliters of the standard sodium fluoride solution are measured into another bottle, 1 ml. of 5 per cent gelatin solution is added with a pipet to each solution, 10 ml. of 95 per cent alcohol are run into each solution, and the bottles are swirled. Five milliliters of the precipitant are then added, the solution being swirled during the addition of precipitant. The bottles are then stoppered and shaken vigorously, and the suspensions allowed to stand 15 minutes.

The nephelometer cups are then rinsed with the standard suspension, and the standard placed on both sides of the instrument. The left side is set at a definite reading, 10 or 20, the lamp turned on, and the right side adjusted to equal intensity of light. A series of six or more readings of the right side is taken, and the right side set at the average of these readings. This setting of the right side is retained for the whole series of comparisons with the standard, being potentially equal to the setting of 10 or 20 on the left side of the instrument.

The standard solution in the left cup is discarded, and the cup is rinsed with unknown suspension, filled with the unknown suspension, and replaced in the instrument. The left side is adjusted to equality of light with the right, four or more readings being taken.

The average of these readings is the comparison of the unknown with the definite setting of the standard (10 or 20). The approximate concentration of the unknown is read from the determined curves (Figures 2 and 3) which give the readings for different concentrations of fluoride compared with a setting of 10 for the standard in Figure 2 and of 20 for the standard in Figure 3.

This preliminary figure having been obtained, a part of the original unknown solution is diluted with sodium chloride solution (55 grams per liter) to about the same strength in fluoride as the standard. An aliquot of this solution is precipitated and compared nephelometrically, as described above,

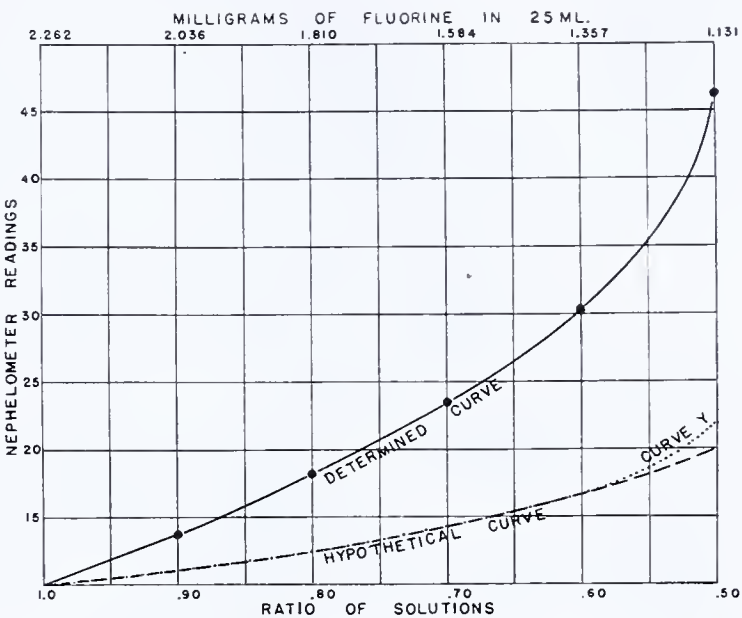


FIGURE 2. NEPHELOMETRIC CURVE FOR DILUTE SOLUTIONS

with a standard suspension prepared at the same time. In the final comparison the unknown should be within about 5 per cent of the standard. Usually two comparisons suffice. If the original unknown solution is weaker in fluoride than the standard, the standard must be diluted to the proper concentration for the final comparison; however, a dilution of the standard to less than one-third strength is not practicable.

The fluoride concentration of the final diluted unknown solution is read from the nephelometric curve and, knowing the dilution, the quantity of fluorine in the sample is calculated.

Determination of the Nephelometric Curves

In the determination of the nephelometric curves the standard was diluted with sodium chloride solution (55 grams per liter) to 90, 80, 70, 60, and 50 per cent and comparisons were made with a definite setting of 10 for the undiluted standard. Knox gelatin was used as a protective colloid and the precipitant was added with a pipet draining in 17 seconds. The values obtained are given in Table I.

TABLE I. COMPARISON OF MORE DILUTE SOLUTIONS TO STANDARD					
(Standard = 2.262 mg. of fluorine per 25 ml. Standard set at 10.0)					
Standard diluted to	90%	80%	70%	60%	50%
Dec. 14	...	17.99	23.28	30.39	46.75
	...	18.23	23.42	30.29	46.82
Dec. 17	14.20	...	24.78	...	49.47
	13.88	...	24.79	...	49.00
Dec. 18	14.00	...	22.12	...	43.09

These values are plotted in Figure 1. They fall precisely on the curves, but the three curves show a slight difference in slope. This difference is in part due to a slight error in comparison of standard to standard, by which the right side of the instrument is set at a value equal to 10 on the left side. This error would become magnified in comparing the less concentrated solutions. For accurate work the unknown and standard should be within 5 per cent of equality in fluoride concentration, the curve serving as a means of approximating the proper dilutions to be made.

In Figure 2 these values and some others are averaged to give an average determined curve. The determined curve is much above the hypothetical, in which readings are assumed inversely proportional to concentrations. This is not objec-

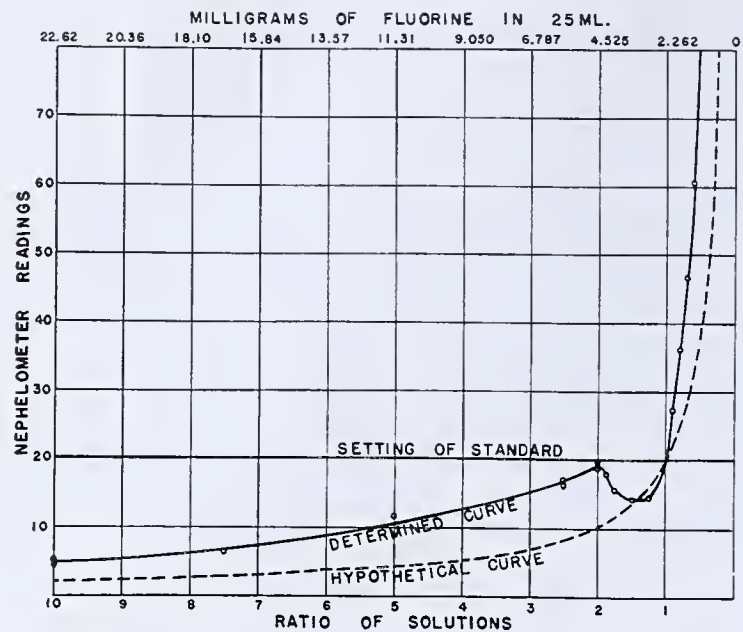


FIGURE 3. NEPHELOMETRIC CURVE FOR CONCENTRATED SOLUTIONS

tionable, provided the readings are reproducible, as they are shown to be. Indeed, the steepness of the curve makes it possible to obtain a much more accurate figure for fluorine with the average observer's sensitivity to light. Curve Y is obtained by dividing the difference between the observed reading and the setting of the standard by three and adding this figure to the setting of the standard. It follows the hypothetical curve closely and was found useful in calculating results.

attained. This time interval was arbitrarily taken and a shorter period may be found sufficient.

The results were obtained at a room temperature of about 22° C. If the standard and unknown are at the same temperature, variations in room temperature would presumably have little effect.

Effect of Rate of Addition of Precipitant

In Figure 4 is shown the result of slower addition of the precipitant. With a 5-ml. pipet that drains in 47 seconds the curve is definitely lower than that obtained when the precipitant is added with a pipet draining in 17 seconds. If the precipitant is added dropwise or the fluoride solution is added to the precipitant, results showed that the weaker fluoride solution may have greater light-reflecting power than the stronger.

Stability of Suspensions

A suspension was prepared from the standard solution at 9:30 A. M. and kept in a glass-stoppered bottle. At 3:30 P. M. a second suspension was prepared. Comparison in the nephelometer showed that the first suspension was 97.8 per cent of the second, a comparatively small change for a 6-hour period.

Duplication of Results in Absence of Interfering Elements

More concentrated solutions are compared to the standard in Table II, and the values are plotted in Figure 3. The curve is useful in determining the dilution necessary to make the unknown and the standard of approximately the same strength for a second comparison. Some uncertainty was experienced in determining these values because of the difference in appearance of the two solutions in the nephelometer. Solutions twice standard and stronger showed a clear sky-blue in the nephelometer, whereas the standard in comparison was a creamy yellow.

In order to determine the accuracy of the method in the absence of interfering elements (sulfates, phosphates, and arsenates) eleven suspensions were prepared from the standard solution and compared in turn with one selected for reference. Ten readings were taken of the reference standard, and four of each succeeding suspension. (See Table III.)

The results show a high precision for nephelometric work (12, 19). Comparisons with preparation 1 were made continuously in the order left to right across the table, and the poorest results, those on preparations 6, 7, and 8, seem to be caused by a temporary eye strain rather than by an error in the preparation of the suspensions.

Errors Due to Maladjustment of Sodium Chloride Concentration

Mistakes in adjusting the sodium chloride content of the solutions result in small errors; if the sodium chloride concentration is too high the results are slightly low, and vice versa. The standard for the tests contained 1.697 mg. of fluorine in 25 ml. and the concentration of 55 grams sodium chloride per liter. A solution containing the same quantity of fluorine but with a sodium chloride concentration of 69 grams per liter gave 98.2 per cent recovery. Another having 41 grams sodium chloride per liter gave 103.3 per cent recovery. By recording the approximate quantity of sodium carbonate used in the extraction, the proper dilution is made to give a concentration of 55 grams of sodium chloride per liter, small differences in sodium chloride content having little effect.

TABLE II. COMPARISON OF MORE CONCENTRATED SOLUTIONS TO STANDARD

(Standard = 2.262 mg. of fluorine per 25 ml. Standard set at 20.0)

Strength compared to standard	1.25	1.5	1.75	1.875	2	2.5	5	7.5	10
Readings	14.6	14.5	15.7	18.1	19.5	16.4	11.9	6.6	4.5
	..	14.5	18.8	16.3	11.9	6.7	4.6
	17.2

PROTECTIVE COLLOID. The curves shown were obtained by using Knox gelatin as a protective colloid. With Difco gelatin the curves were nearer the hypothetical. It is advisable for each observer to determine the nephelometric curves before proceeding to unknown samples.

TIME AND TEMPERATURE. Fifteen minutes were allowed after the addition of the precipitate for equilibrium to be

TABLE III. DUPLICATION IN PREPARING AND READING STANDARD SUSPENSIONS

(Preparation 1 taken as standard and set at 20.0)

Preparation No.	2	3	4	5	6	7	8	9	10	11
Reading	20.25	20.03	20.05	20.08	20.42	19.45	20.78	19.90	20.22	19.92
Calculated hypothetical reading	20.08	20.01	20.02	20.03	20.14	19.82	20.26	19.97	20.08	19.97
Per cent recovery	99.6	100.0	99.9	99.9	99.3	100.9	98.7	100.2	99.6	100.2

Average per cent recovery, 99.8
Greatest deviation from 100 per cent recovery, 1.3 per cent
Average deviation from 100 per cent recovery, 0.4 per cent

Effects of Interfering Substances

Some effects of sulfates, phosphates, arsenates, and ammonium salts on the results are shown in Table IV. Sulfate was added as anhydrous Na₂SO₄, phosphate as KH₂PO₄, and arsenate as Na₂HAsO₄·12H₂O.

TABLE IV. EFFECT OF INTERFERING SUBSTANCES

Fluorine Gram	Fluorine on 2-Gram Sample %	Interfering Substance Gram	Interfering Substance on 2-Gram Sample %	Recovery Shown by Nephelometer Reading %	Fluorine Found %
0.01629	0.81	0.021 SO ₃	1.0 SO ₃	99.3	0.80
0.01086	0.54	0.021 SO ₃	1.0 SO ₃	103.3	0.56
0.01086	0.54	0.021 SO ₃	1.0 SO ₃	103.0	0.56
0.01358	0.68	0.008 P ₂ O ₅	0.4 P ₂ O ₅	121.5	0.83
0.01810	0.91	0.0005 As ₂ O ₅	0.03 As ₂ O ₅	106.5	0.97
0.01358	0.68	0.02 NH ₄ Cl	...	100.4	0.68

The results in Table IV show that the quantity of sulfate taken causes a slight plus error when the fluoride content of the sample is low, but its effect is negligible when as much as 0.80 per cent of fluorine is present in a 2-gram sample. This is due to the steep nephelometric curve for fluorine, the slight turbidity caused by co-precipitation of sulfate being noticeable only in weakly turbid solutions. A large positive error results in weak fluoride solutions when a little phosphate is present, but this likewise would be less for high percentages of fluorine. A small quantity of arsenic causes an appreciable error. Failure to remove ammonium salts completely seems to have little or no effect.

The precipitation with zinc to remove the last traces of silica, in the Berzelius method of extraction, does not remove the phosphate sufficiently. A solution containing 0.0152 gram of phosphate and 0.01358 gram of fluorine in 200 ml. gave 108.8 per cent recovery after the zinc treatment; and a solution having the same quantity of phosphate and 0.00905 gram of fluorine gave 128 per cent recovery. A fairly satisfactory method of removing this quantity of phosphate was to add 1 ml. of 0.1 M ferric chloride before precipitation with zinc oxide, but no method was found for removing phosphate so completely as to cause no interference in the fluorine determination.

Sulfates may be removed with barium chloride. An excess must be carefully avoided, however, as it leads to high results for weak fluoride solutions and removes fluorine when the fluoride content is high, as illustrated by the high and low

results in the middle section of Table V, where barium chloride was used in the absence of sulfate.

Arsenic may be satisfactorily removed by adding about 0.5 gram of 20-mesh metallic zinc before the addition of zinc oxide. During boiling to remove ammonia, the metallic zinc reduces arsenates and at the same time prevents bumping.

Results obtained after using these treatments to remove interfering elements are given in Table V.

TABLE V. REMOVAL OF INTERFERING ELEMENTS

Treatment of Solution	Wt. of Fluorine Gram	Fluorine on 2-Gram Sample %	Interfering Substances Gram	Interfering Substance on 2-Gram Sample %	Recovery Shown by Nephelometer Reading %	Fluorine Found %
Metallic zinc (ZnO)	0.01810	0.91	0.0027 As ₂ O ₅	0.14 As ₂ O ₅	101.2	0.92
	0.01358	0.68	0.0027 As ₂ O ₅	0.14 As ₂ O ₅	100.6	0.68
	0.00905	0.45	0.0027 As ₂ O ₅	0.14 As ₂ O ₅	101.9	0.46
	0.00905	0.45	0.0027 As ₂ O ₅	0.14 As ₂ O ₅	100.4	0.45
	0.01358	0.68	None	None	100.0	0.68
5 ml. of 2% BaCl ₂	0.01810	0.91	None	None	100.9	0.92
	0.01810	0.91	0.021 SO ₃	1.1 SO ₃	100.9	0.92
	0.00905	0.45	None	None	151.0	0.68
	0.00905	0.45	None	None	171.5	0.77
	0.00905	0.45	0.021 SO ₃	1.1 SO ₃	100.1	0.45
	0.04525	2.26	None	None	96.8	2.19
	0.04525	2.26	0.021 SO ₃	1.1 SO ₃	97.8	2.21
FeCl ₃ -ZnO, 5 ml. of 2% BaCl ₂	0.00905	0.45	0.021 SO ₃	1.1 SO ₃	106.2	0.48
			0.004 Cr ₂ O ₃	0.2 Cr ₂ O ₃		
			0.008 P ₂ O ₅	0.4 P ₂ O ₅		
	0.01358	0.68	0.021 SO ₃	1.1 SO ₃	102.0	0.69
			0.004 Cr ₂ O ₃	0.2 Cr ₂ O ₃		
			0.008 P ₂ O ₅	0.4 P ₂ O ₅		
	0.1810	9.05	0.021 SO ₃	1.1 SO ₃	100.3	9.08
			0.004 Cr ₂ O ₃	0.2 Cr ₂ O ₃		
			0.008 P ₂ O ₅	0.4 P ₂ O ₅		
	0.0905	4.53	0.021 SO ₃	1.1 SO ₃	100.1	4.53
			0.004 Cr ₂ O ₃	0.2 Cr ₂ O ₃		
	0.1810	9.05	0.008 P ₂ O ₅	0.4 P ₂ O ₅	97.8	8.85
			None	None		

Failure of Method for Phosphate Minerals

The method was not found satisfactory for materials of high phosphate content, owing to incomplete extraction of fluorine (9) and to failure to remove all the phosphate. For known solutions of high phosphate content, two precipitations with a large excess of zinc oxide gave slightly high results for fluorine. Two precipitations with 1 ml. of ferric chloride in combination with zinc oxide were better, but caused the loss of a small portion of the fluorine when present in large quantity. A higher concentration of hydrochloric acid in the precipitant might prevent the co-precipitation of phosphate, but would probably change the nephelometric relationships.

The results obtained on some phosphates, after removal of phosphate by two treatments with ferric chloride and zinc oxide, are given in Table VI. The fluoride solution obtained from triplite failed to follow the nephelometric curve on dilution, showing that the phosphate was not completely removed. The figure given for the fluorine in triplite, therefore, is probably high. The tests on phosphate rock seem to show incomplete removal of fluorine.

TABLE VI. DISCREPANCIES WITH PHOSPHATE MINERALS

Sample	Locality	Fluorine Found %	Fluorine by Other Methods %
Triplite	Amelia, Va.	9.76	9.58 ^a 8.93 ^b
Phosphate rock	Wyoming	2.83	3.58 ^c
Phosphate rock	Tennessee	2.93	3.75 ^c
Phosphate rock	Florida	3.14	3.89 ^c

^a J. G. Fairchild by volumetric.
^b J. G. Fairchild by Berzelius.
^c Distillation, Reynolds, Ross, and Jacob

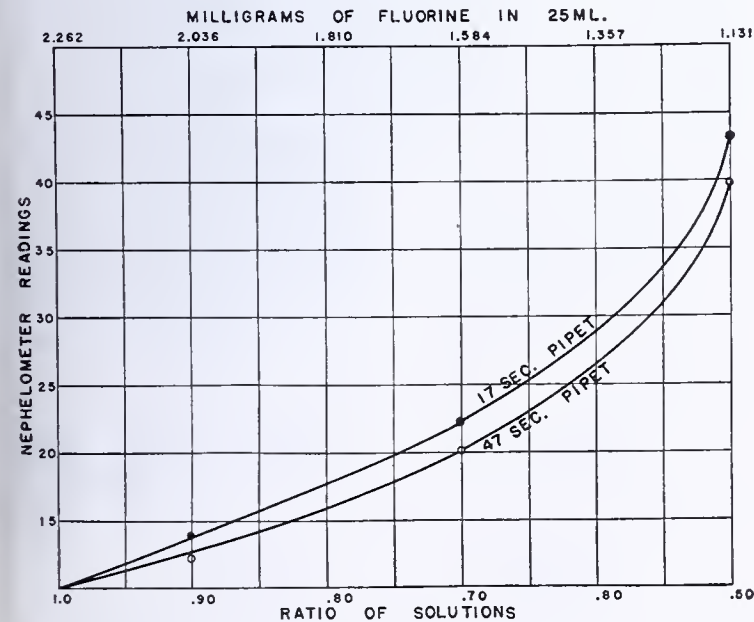


FIGURE 4. EFFECT OF RATE OF ADDING PRECIPITANT

Results with the Method

In Table VII are given determinations on silicates and fluorine-containing minerals. The two results on phlogopite check closely; no theoretical figure for fluorine is given, as the fluorine content of phlogopite varies. Results on gearsutite and creedite are much closer to the calculated theory than previous determinations. Bureau of Standards standard sample 91 gave a figure in fair agreement with the result obtained by Hoffman with the lead chlorofluoride method. In topaz hydroxyl replaces fluorine, so that no theoretical figure for fluorine is given. The topaz listed is unusual in having a high water content (2.67 per cent of combined water)

TABLE VII. RESULTS WITH THE METHOD

Sample	Locality	Fluorine Found %	Theory	Results by Other Methods
1. Phlogopite	Kings Mountain, N. C.	4.31 4.34
2. Fluorite	Rosiclare, Ill.	48.65	48.68
3. Gearsutite	Wagon Wheel Gap, Colo.	42.30	42.9	Average of results by three different analysts using Berzelius method, 41.2
4. Creedite	Wagon Wheel Gap, Colo.	30.96	30.9	R. C. Wells by difference, 30.35
5. Bureau of Standards standard sample 91, opal glass	5.83	...	J. I. Hoffman by lead chlorofluoride method, 5.75
6. Topaz	Jefferson, S. C.	13.23

and hence a low fluorine content (13.23 per cent). The complete analysis gave a summation of 100.13, after subtracting the oxygen equivalent of the fluorine.

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Microvaporimetric Determination of Molecular Weight

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IN 1929 Niederl (26) described a simple microvaporimetric method for the determination of the vapor density or the molecular weight of low-boiling liquids. This method was improved (29) so that the results were within ± 2 per cent of the theoretical (24, 27); consequently, its application to higher boiling substances for temperatures up to 200° C. was investigated (28). But the difficulty of obtaining temperature constancy increased proportionally with the rise in temperature, so much so that such improvements as a fused-in thermometer and other suitable changes in apparatus did not appreciably increase the accuracy of the results. Further experimental studies finally led to the development of a method for temperatures up to 320° C., retaining all the favorable features of the low-temperature method, such as visual observation of the boiling and condensing point, as well as repetition, and to the construction of the improved,

yet extremely simple and inexpensive apparatus as set forth in this communication.

Principle of the Method

A few milligrams of a substance, either liquid or solid, are vaporized in a closed system in such a way as to permit an accurate indirect volume determination with suitable provisions for pressure and temperature control and constancy at any point for a temperature range of 300° C.

The method is not merely a miniature macromethod, but may be compared with the classical vapor density macromethods of Hofmann (16) and Meyer (22). Mercury, the sealing fluid, is displaced instead of air as in the older method. Both methods (9, 11, 32) and to a lesser degree their many modifications (3, 5, 6-8, 10, 15, 18, 20, 21, 23, 30) as well as the vapor density method of Dumas (12) and others (31)

The previously described micromethod for determining vapor density of low-boiling liquids has been suitably modified to include high-boiling liquid and solid substances of various types. The results obtained compare favorably with any of the existing macro- or micromethods based upon similar principles. The method, in addition to the determination of the molecular weight, permits repetition as well as simultaneous observation of the boiling and condensing point on a single sample of a few milligrams in weight.

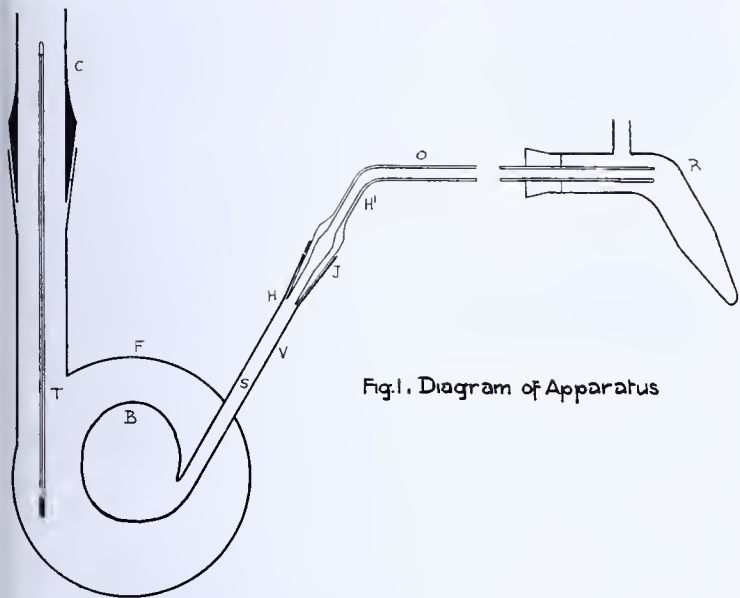


Fig. 1. Diagram of Apparatus

have found their application in quantitative organic micro-analysis (4).

Apparatus

The apparatus consists of a round-bottomed Pyrex flask, *F*, which is 7 to 8 cm. in diameter and has a capacity of about 350 cc. Its neck (7 to 8 cm. long) is not in the center but tangent to the flask surface and has an inner diameter of about 2 cm. By means of an interchangeable ground-glass (No. 15) joint either a Liebig water condenser or a plain air condenser, *C*, of inner diameter large enough (10 to 12 mm.) to permit the insertion of a thermometer, *T*, and about 50 cm. in length, is connected to the flask, which serves as the container of the bath liquid. The Pyrex glass vaporimeter, *V*, consists of the vaporizer which has the shape of a slightly elongated (egg-shaped) bulb, *B*, of from 12- to 15-cc. capacity and the hollow stem, *S*, which is 11 cm. long. Its inner diameter is 6 mm. The glass bulb, *B*, is attached to the hollow stem, *S*, at an angle of about 45°. It is important that the inner diameter of the bend between the vaporizer and the stem be slightly larger (7-mm. inner diameter) than the inner diameter of the rest of the stem. The capillary outlet tube, *O*, is also bent at an angle of 45° and has an outer diameter of 5 mm. and an inner diameter of 2 mm. Its horizontal arm is about 10 cm. long, while its oblique arm together with the interchangeable, hollow ground-glass joint, *J* (No. 5), is 5 cm. long.

Between this glass joint and the bend there are also two glass hooks, *H'*, for the attachment of steel springs leading to the glass hooks of the stem, thus preventing any loosening of this connection during the experiment. The entire vaporimeter, *V*, which thus assumes the form of a curved pipe, is fused into the heating flask opposite its neck at an angle of about 45° in such a manner that the glass bulb, *B*, is fairly in the center of the heating flask, *F*. The orifice of the ground-glass joint extends at least 5 cm. above the heating jacket. The thermometer, *T*, is introduced through the condenser, *C*, into the bath liquid and is held in position by means of a fine flexible wire. A centrifuge tube of about 15-cc. capacity, which is bent downward below the side arm at an angle of about 45°, serves as the receiver, *R*, for the displaced mercury. By means of a suitably bent wire this receiver is attached to the top hook of the weighing pan of the analytical balance. This and all the previously described apparatus were made by Eck and Krebs, 131 West 24th St., New York, N. Y., who together with Eimer and Amend, Third Ave. and 18th St., New York, N. Y., are able to supply these instruments at reasonable cost.

Reagent

The mercury used as the sealing liquid must be free from volatile substances. Of the many purification procedures for mercury, the following was found to be entirely adequate:

Mercury (commercial, c. p., or reclaimed) is allowed to fall in a fine stream through a column of dilute nitric acid (10 per cent) or concentrated sulfuric acid. After separation it is treated in a similar manner with water, then with acetone and finally again with distilled water. After separation, the mercury is placed in

a thick-walled round-bottomed flask and while attached to a water suction pump it is heated in an oil or sand bath to 250° C.

Preparation of the Sample

SOLIDS. Soft-glass capillaries not less than 1.5 mm. in inner diameter are prepared by drawing out either soft-glass test tubes in a blast lamp, or soft-glass tubing in a wing burner. These capillaries are then cut to about 8 to 9 cm. in length (Figure 2, No. 2). One of the capillaries, the outside of which is cleaned by drawing it through a clean piece of cotton fabric, is weighed to the nearest 0.001 mg. The reproducibility of the weighings need not be greater than ± 0.005 mg., and any microchemical balance showing this sensitivity at a load of from 0 to 1 gram can be used for this determination. Such capillaries weigh usually about 150 to 200 mg. and are counterpoised by either another capillary or the standard weights.

The solid substance to be analyzed is now melted on a microscope slide, on a watch glass, or in a capillary of wider bore. The weighed capillary is brought into contact with the molten substance which by capillary attraction is allowed to rise in the capillary to a height of not more than 4 mm. The capillary with the molten substance, 3 to 9 mg., is then withdrawn and allowed to cool. If no crystallization takes place upon cooling, the capillary is dipped for a moment into the remaining solid sample. After crystallization, the outside of the capillary is cleaned, and it is weighed again as described.

If the substance is a solid, which does not melt but sublimes, the capillary as prepared above is sealed at one end and weighed in this condition (Figure 2, No. 3). The sample is then introduced as in the taking of melting points. To ensure compactness, the capillary is allowed to drop on a glass surface through a vertical glass tubing at least 1 meter in length. Cleaning and weighing of the capillary thus prepared are done as described above.

LIQUIDS. Liquids of high viscosity or semi-solids may be introduced in the same way as crystalline solids, using capillaries open at both ends (Figure 2, No. 2). Otherwise liquids are introduced by means of capillary weighing pipets (1) prepared according to Pregl (33, 34), omitting the potassium chlorate (Figure 2, *a, b, c*). These weighing pipets, however, should be shorter and of wider inner diameter (2 mm.).

Procedure

INTRODUCTION OF THE SAMPLE. The bath liquid is first removed from the flask and placed in a suitable container for re-use, and the flask is stoppered. The capillary outlet tube is detached, by first removing the steel springs and then slowly withdrawing it from the ground-glass joint, holding the apparatus over a trough or other device to collect any spilled mercury. The mercury from the vaporimeter is emptied into a suitable bottle, and at the same time the capillary, which served as the container of the substance, is removed. A little acetone (about 1 to 2 cc.) or other volatile organic solvent is introduced into the vapor-

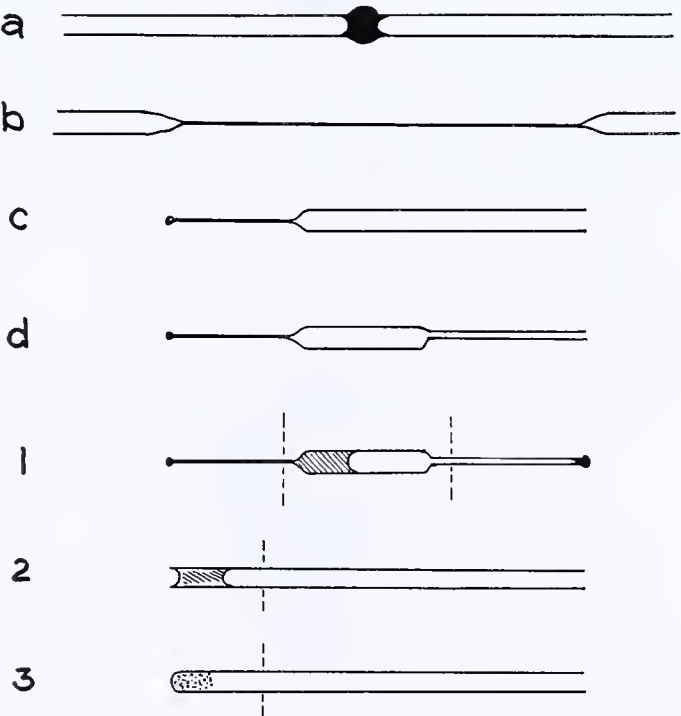


FIGURE 2. WEIGHING CAPILLARIES

imeter, and the apparatus is well shaken, while the opening of the vaporimeter is closed with the finger or a small cork. The solvent is removed and this operation repeated at least three times. The apparatus is then placed in an oven at about 100° C. and while still warm the outlet of the vaporimeter is attached to a suction pump to ensure the complete removal of the solvent. The sample to be analyzed is introduced into the cooled apparatus as follows:

Solids. The weighed capillary, open at one or both ends, is cut about 2 mm. above the substance. This section of the capillary, the entire length of which should not be more than 8 mm. (Figure 2, Nos. 2 and 3), or short enough so that it can pass the bend of the vaporizer, is allowed to slide into the bulb of the vaporimeter.

Liquids. The stem of the capillary pipet is cut off just below the center bulb, and the pipet is centrifuged to remove all liquid from its hair-fine end. While the pipet is held at this hair-fine ending, it is cut just above the center bulb (Figure 2, No. 1) and the bulb containing the substance is allowed to slide into the vaporizer. Special precautions are necessary for very volatile liquids, such as diethyl ether, divinyl ether, acetaldehyde, etc. In this case, previous to the introduction of sample, ice water is introduced into the flask which is then stoppered. The mercury and the sealed and weighed capillary are cooled similarly.

FILLING THE APPARATUS. Mercury, cleaned and dried as described above, is poured into the vaporimeter while the entire apparatus is held or placed in a suitable trough. This filling operation is accomplished with a minimum of spilling by using a Kells-Ringer flask or similar device having double outlets, one of which has a fine opening. By proper tilting of the flask, the entire bulb and then the entire stem up to the ground-glass joint are easily filled with mercury. The joint of the capillary outlet tube is greased lightly and the tube is inserted into the stem of the vaporimeter, thus filling the outlet tube with mercury to about one-third. The steel springs are then attached. The outlet tube is filled completely with mercury by means of a pipet, prepared by drawing out an ordinary glass tubing to a capillary, fine enough so that it fits about 2 cm. into the capillary outlet tube. This pipet has a rubber cap and by proper inflation a small amount of mercury is drawn into the pipet. The pipet is then inserted into the capillary outlet tube and a small amount of mercury introduced by the application of pressure to the rubber cap. The column of mercury so introduced can be made to join the mercury column in the capillary outlet tube by introducing and withdrawing a fine wire (copper, platinum, etc.). Repetition of this operation soon fills the outlet tube completely with mercury. Finally, the weighed receiver is attached to the capillary outlet as shown in Figure 1 and the entire apparatus is placed on a suitable stand, provided with a ring clamp and wire gauze. The bath liquid is next introduced, and should cover about two-thirds of the bulb of the vaporimeter. Small pieces of porous tile or boiling point capillaries are added and the condenser is attached (air condenser for bath liquids boiling above 170° C.). A thermometer is introduced through the condenser into the bath liquid so that its mercury bulb is completely immersed, and is held in this position by means of a flexible wire (copper, etc.). In order to attain equilibrium of temperature, the apparatus is allowed to remain in this condition for about 5 minutes, after which period the starting temperature, T_1 , is read. Any mercury that may have entered the receiver is removed and the receiver re-attached.

HEATING. After the initial starting temperature, T_1 , has been ascertained, the apparatus is heated rather rapidly up to near the boiling point of the bath liquid. The heating may be accomplished electrically, by applying a free flame, or using suitable heating baths (oil, sand, or Wood's metal bath). As soon as the bath liquid begins to boil, the heating is reduced to a minimum and the boiling is continued for exactly 2 minutes, at which time the thermometer inside the condenser is again read to give the end temperature, T_2 . After this reading the heating is discontinued and the entire apparatus allowed to cool. The receiver containing the displaced mercury is removed and weighed on an ordinary analytical balance to ± 0.01 gram.

CORRECTION FOR HEAT EXPANSION OF APPARATUS. By performing the experiment as described above, but using an empty capillary without a sample, it is possible to determine how much mercury is expelled by heat expansion of the mercury and glass and by other minor factors, $c_1(T_2 - T_1)$, while the apparatus is heated from T_1 to T_2 .

From the amount of mercury displaced at several temperature points (three are sufficient) a graph may be plotted, from which the amount of mercury collected from this particular apparatus may be ascertained for any temperature up to the boiling point of mercury.

Calculation

$$M = 62351 \frac{wt(273.2 + T_2)}{VP}$$

M = molecular weight

wt = weight of sample

T_2 = final temperature

$$V = \frac{g - [c_1(T_2 - T_1)]}{d} - v_s$$

V = volume of vapor

g = weight of displaced mercury

c_1 = correction for expansion per 1° C.

T_1 = initial temperature, ° C.

T_2 = final temperature, ° C.

d = density of mercury at T_2

v_s = volume of the sample $\frac{(\text{weight})}{(\text{density})}$ (approximately 1 cu. mm. per mg.)

$$P = p_1 + p_2 - p_3 + p$$

P = pressure of vapor

p_1 = barometer reading

p_2 = vertical distance in mm. between the mercury meniscus in the vaporizer and the orifice of the capillary outlet tube

p_3 = vapor pressure of mercury at T_2

p = capillary depression of mercury in outlet tube (+ 8 mm.); temperature reduction of barometer (−2 mm. at 15° C., −4 mm. at 32° C.); density reduction of mercury in stem of vaporimeter for that portion of the stem of vaporimeter which is inside of heating chamber (−1 mm. for $T_2 = 100^\circ \text{C.}$, −2 mm. for $T_2 = 180^\circ \text{C.}$, −3.5 mm. for $T_2 = 320^\circ \text{C.}$)

The net value of p is usually small (about +0.5 per cent of P) and within the limits of accuracy and precision of this method, therefore, for practical purposes this correction may be omitted.

TABLE I. TYPICAL MOLECULAR WEIGHT DETERMINATIONS

(Results obtained by students while learning the method, 25)

Substance	Bath Liquid	Weight Mg.	V Cu. mm.	T_1	T_2	P	Molecular Weight Found	Theoretical
Methyl alcohol	Water	5.556	4.585	25	100	852	33	32
Ethyl alcohol		4.552	2.666	25	100	852	46	46
Bromobenzene	<i>p</i> -Cymene	3.047	0.625	27	180	839	164	157
Propionic acid		2.779	0.729	24	180	850	128	130
anhydride		4.533	1.372	31	269	730	153	156
Menthol	α -Naphthyl methyl ether	6.062	2.135	28	267	750	128	128
Naphthalene		7.899	2.449	28	268	740	147	150
Thymol		10.125	4.007	25	268	764	110	108
Benzyl alcohol	Benzyl ben- zoate	9.170	4.016	29	318	499	169	169
Diphenyl amine		3.096	1.952	25	319	503	119	122
Benzoic acid								
c_1 , 0.028 gram of mercury								
° C.			d (19)			p_3 (19)		
100			13.352			9		
180			13.160			123		
270			12.947			368		
320			12.829					

Further Modifications of Method

Although the vapors of the substance are not in contact with air, a fact which lessens the danger of possible oxidation, they are under a pressure greater than atmospheric (about 100 mm.). This pressure, however, may be diminished through partial evacuation, by attaching the side arm of the receiver to a suction pump with provision for the maintenance of a constant although lower pressure (300 mm., etc.). The determination may be repeated on the same sample by attaching a side-arm test tube containing sufficient mercury to the orifice of the capillary outlet tube at the end temperature, T_2 , and allowing the apparatus to cool. After cooling, an

equivalent amount of mercury, which can be determined quantitatively, is drawn back into the apparatus. The filling of the vaporizer may be carried out also by evacuation of the vaporimeter already containing the nonvolatile sample and by suitable arrangement allowing mercury to enter this portion of the apparatus. The boiling and condensation points, which can be simultaneously observed and ascertained, are comparable with the results obtainable with other micro-methods already known (2, 5, 13, 14, 17, 35-38), corrections for the higher pressure, p_1 and p_2 , being necessary. By slightly enlarging the bulb (vaporizer) of the vaporimeter without changing the apparatus otherwise, larger samples (10 to 20 mg.) can be used which need to be weighed only to ± 0.05 mg., a precision obtainable with any good macro-chemical balance, eliminating the use of a microchemical balance.

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Saponification Numbers of Asphaltic Petroleum Residues

Pressure-Agitation Method

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THE determination of the saponification numbers of the black asphaltic residues encountered in the petroleum industry is a procedure which is well known to be fraught with difficulties. Methods too numerous for reference have been devised. The most successful procedure has been that of adding benzene to the sample (1), which renders it soluble throughout the saponification and results in a two-layer titration medium, the end point of which can be seen with fair accuracy by means of a titration pipet (3). However, in order to obtain complete saponification it is sometimes necessary to boil the benzene-alcoholic solution under reflux for an undue length of time. Furthermore, the benzene layer, in which is dissolved the dark-colored material, remains on top of the lighter colored layer which contains the excess alkali and must be titrated. These disadvantages made apparent the need for a method whereby the time required for a complete saponification could be shortened and a dissolving medium employed which not only would be miscible with the asphaltic material, but also would become viscous enough at titration temperatures to hold it at the bottom of the flask.

Analytical Procedure

A weighed sample of the heavy semi-solid asphaltic residue is mixed with a known amount (about 1 to 2 parts) of white oil,

paraffin oil, or similar oil (viscosity about 80 to 85 seconds Saybolt at 54.44° C., 130° F.). A liquid mixture is obtained which may be conveniently handled by means of a medicine dropper. About 3 to 4 grams of this mixture are weighed into an ordinary glass pressure flask, 50 to 100 ml. of 0.05 *N* anhydrous alcoholic potassium hydroxide are added, and the flask is placed in a shaking device (Figure 1) where it is agitated at 100° C. for 30 to 60 minutes. At this temperature the viscosity of the asphalt-white oil mixture is greatly reduced, with the result that a more

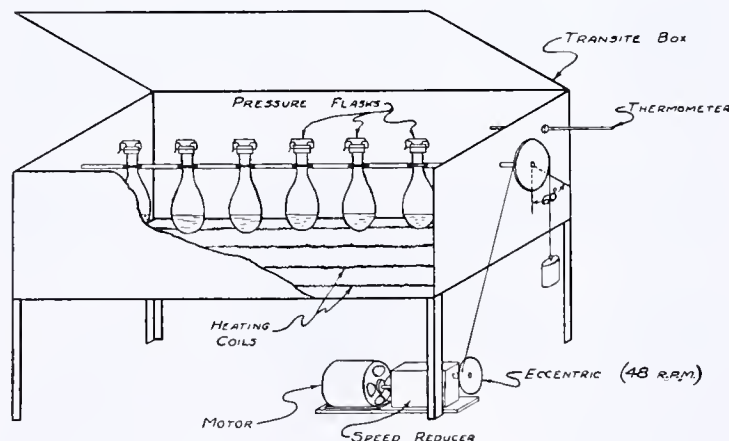


FIGURE 1. SHAKING DEVICE

TABLE I. SAPONIFICATION NUMBERS DETERMINED BY THE PRESSURE-AGITATION METHOD

Sample		Saponification Number Found
Crude petroleum acids from still bottoms (black)	1	38.6
	2	38.8
	3	38.8
	4	39.0
	Av.	38.8
Acidified residues from lubricating oil distillations (black)	1	16.0
	2	16.8
	3	16.8
	4	16.6
	5	14.8
	Av.	16.2
Oleic acid (saponification No. 193.2 by standard method)		193.0
Stearic acid (saponification No. 196.8 by standard method)		197.0
China wood oil (saponification No. 193.0 by standard method)	1	202.0
	2	204.0
	3	202.0
	Av.	202.6
Cottonseed oil (saponification No. 210 by standard method)	1	221.0
	2	219.0
	3	218.0
	4	222.0
	Av.	220.0
Neats'-foot oil (saponification No. 193.0 by standard method)	1	202.0
	2	200.0
	3	203.0
	Av.	202.3

intimate contact is obtained with the alcoholic layer. This contact between the two layers is obviously increased more than a hundred fold by the continuous agitation.

Upon cooling to room temperature (without agitation), the saponified black residue becomes very viscous and sticks to the bottom of the pressure flask, while some of the white oil remains dissolved in the alcohol layer. Thus, in spite of the excellent contact afforded between the alcoholic and the asphaltic layers during the saponification, the solubility of the black material in the alcohol layer remains sufficiently small to prevent serious discoloration of the top layer. Hence, the supernatant alcoholic layer may be poured from the pressure vessel into an Erlenmeyer flask or a white casserole and titrated with 0.1 *N* hydrochloric

acid, using phenolphthalein or alkaline blue as an indicator. When the end point has been reached, some of the liquid from the titration container is carefully poured back into the pressure flask and the black residue on the inside of the flask is washed with this neutral liquid. The rinse is then returned to the casserole and a new end point is determined. The black insoluble residue, therefore, remains in the pressure flask and is thus kept entirely separate from the alcoholic layer during the titration. In order to obtain a yellowish or a light brownish color of the solution prior to the titration, it is important to add only moderate amounts (1 to 2 parts) of white oil to the asphalt.

Among the advantages of the suggested method the following may be mentioned:

1. The determination of the exact end point is greatly facilitated, since the titration is carried out in the absence of the saponified black residue.

2. Even for residues of the highest viscosities and molecular weights, a complete saponification is obtained in 30 to 60 minutes because of the continuous mechanical agitation and higher temperatures employed.

3. Since the saponification is being conducted in a closed system, interference of atmospheric carbon dioxide is eliminated, losses of low-boiling esters are prevented, and errors known to be contributed (2) by cork stoppers are avoided.

Results Obtained

Some of the results obtained by the new method are given in Table I.

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Determination of Iron in Humates

Use of Iodohydroxyquinolinesulfonic Acid

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THE determination of iron in small quantities in organic material involves two procedures: (1) the oxidation of the organic matter, and (2) the determination of the iron, usually colorimetrically. The removal of the carbon may be carried out by heating (the dry method) or by a wet oxidation. The colorimetric determination most frequently involves potassium thiocyanate; comparison is made between the unknown and a standard iron solution similarly treated. The color produced by the iron and the thiocyanate fades, and fresh standard solutions must be made up at frequent intervals.

In carrying out the dry oxidation of the organic matter in humate material from soils, followed by the potassium thiocyanate determination, some difficulty was experienced in obtaining checks. Burk (1) has pointed out the value of these humic acid extracts from soils, and also of synthetic humates formed from carbohydrates, as carriers of iron, and has shown the availability of this iron to green plants even under alkaline conditions. In inorganic combination iron hydrolyzes very slowly at about pH 3, but at pH 5 and above ferric hydroxide is precipitated more rapidly. Unlike iron in the inorganic form, the iron in the humic acid extracts and in the synthetic humates does not precipitate at pH 5; there

is no hydrate of ferric oxide formed, even to pH 8 or 9; the iron, therefore, remains in solution over the ordinary plant growth range.

Iron can be added to the humate extracted from soils and is either adsorbed or combined; this added iron does not precipitate at pH values greater than 5. In a number of experiments along these lines (2) the authors found it necessary to determine very accurately the quantity of iron in the humate before and after enrichment with that element. Results by the dry oxidation of the carbon followed by the potassium thiocyanate were irregular, and iron added as a check was not always completely recovered.

In 1932, Yoe suggested 7-iodo-8-hydroxyquinoline-5-sulfonic acid, $C_9H_4N(OH)I(SO_3H)$, as a reagent for the colorimetric determination of iron (4). The name "Ferron" has been proposed for the indicator (3). With this dye, which is obtainable commercially, ferric iron gave a green color and ferrous did not react. A concentration of 1 in 10 million gave a greenish yellow, with higher amounts more green. The color was very stable, and therefore it was not necessary to prepare standard and sample at the same time as with the thiocyanate. Yoe found that the color developed best when the solution was acid to methyl orange paper. He tested some

TABLE I. IRON IN POTASSIUM HUMATE

Amounts Oxidized Potassium humate	Standard Fe, 2 mg. per liter	pH ^a		Total Iron Present		Blank	Fe in Sample	Fe in Humate Solution
		0.1 N KOH to bring 10-cc. aliquot to pH 2.75-3.2	0.1 N KOH for 25-cc. aliquot (calcd.)	Standard Fe (2 mg. per liter) to match 25-cc. aliquot ^b	Fe in 70-cc. oxidized solution			
Cc.	Cc.	Cc.	Cc.	Cc.	Mg.	Mg.	Mg.	Mg./cc.
0	50.0	11.7	29.2	19.0	0.106	0.006	0.100
0	50.0	12.7	31.7	19.0	0.106	0.006	0.100
0	50.0	13.5	33.7	19.0	0.106	0.006	0.100
50.0	0	10.6	26.5	7.0	0.039	0.006	0.033	0.0007
50.0	0	9.3	23.2	7.0	0.039	0.006	0.033	0.0007
50.0	0	9.8	24.5	7.0	0.039	0.006	0.033	0.0007
25.0	25.0	11.1	27.7	13.0	0.073	0.006	0.067	0.0007
25.0	25.0	11.4	28.5	13.0	0.073	0.006	0.067	0.0007
25.0	25.0	12.3	30.7	13.0	0.073	0.006	0.067	0.0007

^a Potassium hydroxide added until faint blue to bromophenol blue when diluted to 40 cc. 0.8 cc. 0.1 N sulfuric acid brought this to pH 2.75 to 3.2. The difference, multiplied by 2.5, gave the net cc. of potassium hydroxide to be added to the 25-cc. aliquot before making up to 100 cc. for the Nessler tube.
^b Diluted to 100 cc. at pH 2.75 to 3.2; 1 cc. of color reagent, 0.2 per cent.

70 other ions and obtained no color. Cupric ion produced a precipitate, and a few salts which hydrolyze, such as tin and titanium, needed removal if present in more than very small amounts. Strong acids and bases destroyed the color.

Combined Method

It was decided to combine this method with the wet oxidation, by means of hydrogen peroxide, which Koch and McMeekin used for micro-Kjeldahl determinations. (A mixture of perchloric and nitric acids should prove equally effective as an oxidizing agent for removing the organic matter, as it is improbable that the nitrate or perchlorate ions would affect the green color.) The side arms of small Pyrex distillation flasks were sealed off and the flasks calibrated to hold 70 cc. The organic material, containing approximately 0.1 mg. of iron, was placed in the flasks with 5 cc. of 10 per cent sulfuric acid, with a bead to prevent bumping, and heated until white fumes came off; after cooling for a minute, a few drops of 30 per cent hydrogen peroxide were allowed to fall directly into the acid, and the heating was continued until the sulfur trioxide condensation was within 5 cm. (2 inches) of the top of the neck. The hydrogen peroxide treatment was repeated if the liquid was not clear. The solution was made up to 70 cc. at 24° C. and aliquots were used for the determination of the iron.

Yoe stated that best results were obtained if the solution was made acid to methyl orange paper. Aliquots were therefore treated with 0.4 N potassium hydroxide until just acid to the paper, and methyl orange was also used as an internal indicator, potassium hydroxide being added until a faint pink color was obtained; the same amount of potassium hydroxide was then added to a second aliquot and the iron determined in this. In both cases the results were somewhat unsatisfactory. There was a large color change in the green produced by the reagent when a slight excess of either potassium hydroxide or acid was present.

In order to find the limits for change in color with acidity, a standard iron solution was made from recrystallized ferrous ammonium sulfate, oxidizing with bromine to the ferric ion, and removing the excess bromine. Varying amounts of sulfuric acid and potassium hydroxide were added and the colors compared. Between pH 2.7 and 3.2 there was a stable green that was constant for each different amount of iron; more alkaline solutions produced a yellow and more acid a blue-green. The blue-green is stable at least to pH 2, but for comparisons, the authors preferred the color produced at the higher value. The standard iron solutions were therefore made up within the pH limits 2.7 to 3.2, and if dilution was necessary it was made with distilled water acidified to the same value. Yoe has suggested a hydrochloric acid-potassium acid phthalate buffer (3).

The treatment of the unknown solutions was also modified to conform with this finding. After digesting the organic matter with sulfuric acid and hydrogen peroxide and making up to 70 cc. a 10-cc. aliquot was removed and 0.1 N potassium hydroxide added until a faint blue color was produced with 2 drops of bromophenol blue as internal indicator, when diluted to 40 cc. with distilled water; 0.8 cc. of 0.1 N sulfuric acid brought this to the range 2.7 to 3.2. The amount of sulfuric acid subtracted from

the potassium hydroxide left the net amount of potassium hydroxide required. A fresh 25-cc. aliquot of the oxidized solution was then used, with two and one-half times the amount of potassium hydroxide found for the 10-cc. sample, and brought exactly to 100 cc. for nesslerization. With the use of a glass electrode to adjust the pH, the indicator is not necessary, but the bromophenol blue method is more rapid.

Test runs were made on a number of materials, including iron citrate and a mixture of iron citrate and sucrose. Table I gives the results for an extract of soil with potassium hydroxide—the potassium humate. The alkali extract of soil contained a small amount of silicate, but this did not interfere, as shown in Table I. To check this further a run was made using the standard iron solution, but adding 0.1 to 1 mg. of silica as sodium metasilicate. The iron was recovered completely at each silicate level.

The standard iron solution, from the ferrous ammonium sulfate oxidized by bromine, deteriorates slowly if the reaction is much greater than pH 2. Two liters were made up at pH 2.9; these were tested, at first daily and later every 2 days, against a freshly oxidized solution. The standard was constant for 3 days, but the ferric ion slowly decreased thereafter. The permanency of the green color, when this standard is treated with the iodohydroxyquinolinesulfonic acid at pH 2.7 to 3.2, is almost indefinite. Solutions were made up containing 0.02, 0.04, and 0.06 mg. of iron in 100 cc., and the green color was produced with the reagent. No change in color was found at any level of iron during the 25 days these were tested against freshly made solutions.

The method seems to be a valuable addition to the colorimetric determination of iron because of this color stability, and because of the fact that there is so little interference by other ions—a very desirable characteristic in dealing with soil extracts.

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CORRECTION. In the article on "Spectrophotometric Determination of Copper in Ores and Mattes" [IND. ENG. CHEM., Anal. Ed., 7, 388 (1935)] the third line should read: "The ratio I_0/I may be evaluated."

J. P. MEHLIG

Measuring the Thickness of Thin, Flowing, Liquid Films

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THE commercial application of ultraviolet radiation in photochemical processes has created new scientific problems. The shallow penetrating power of these rays usually requires that the substance to be treated be distributed in a thin layer. When the substance is a liquid, it is exposed in a thin flowing film. The commercial irradiation of milk to increase its vitamin D potency is an example of such a process. Because of the relatively small amount of activatable substance in milk and the shallow penetrating power of the active radiation, the effectiveness of the process may depend upon the characteristics of the film, and these should be understood.

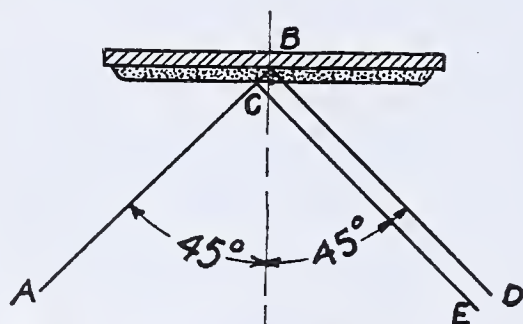


FIGURE 1. DIAGRAM ILLUSTRATING MEASURING THICKNESS OF FILM BY LIGHT BEAM

In a film of known width and capacity, the thickness of any cross section perpendicular to the direction of flow is dependent upon the average velocity of the fluid. When the average velocity of flow within a given distance has been measured, the average thickness of the film within that distance can be calculated. Similarly, when the thickness of a uniform cross section of film has been determined, the velocity of the fluid through the cross section can be calculated. It is possible, therefore, by measurement of the thickness of cross sections at succeeding short intervals to determine any variations in velocity.

Recently, in studies with milk, two methods have been employed for measuring and determining film velocity and/or thickness. A method utilized by Supplee and Dorcas (3) is one wherein the flow is measured with the aid of aggregates of finely divided pigment placed in the film. Application of this method revealed, however, that particles at different depths within the film do not advance at a uniform velocity. Compact groups of particles or drops of suspended colored material placed in a flowing liquid are elongated and dispersed to many times their original dimension by the film in the direction of flow. It was difficult to establish which particles advanced at speeds representative of the average forward velocity of the film. For this reason the method does not lend itself to measurement of acceleration of velocity of a film through consecutive short distances of flow.

The second method (1), employing a screw type of micrometer suitably mounted in a tripod, was also investigated. With this instrument the thickness of the film is the distance measured between contact of the micrometer point with the surface of the liquid film, and the metal surface supporting the film. The advantage of this method is its flexibility which permits measurements to be made at any point on a flowing film; variations in film thickness which may occur between

consecutive points can be detected. However, manipulation of the micrometer causes interference with the normal smooth flow of the film, and undoubtedly some leverage is exerted at contact with the metal surface. These difficulties produce errors which are additive, and probably constant. With suitable recognition of such error the micrometer method might nevertheless serve as a guide in appraising the reliability of other methods.

To overcome the disadvantages of these methods, a new procedure which was found more suitable for measuring the thickness of flowing liquid films was developed.

Description of Method

The method utilizes the well-established principle that some light is reflected from any surface, and that the angles of incidence and reflection are equal (2). Parallel forward movement of the surface causes a proportional change in the position of the reflected beam. The position of the beam of light reflected from the surface will be likewise affected by introducing an interjacent flowing film of liquid. The application of the principle is illustrated in Figure 1.

A very narrow beam of light, AB, is projected onto a metal surface at B at an angle of incidence of 45° whence the angle of the reflection, BD, will also be 45° . If now a uniform film of liquid is made to flow down the metal surface, the beam is reflected from the surface of the liquid at some point, C. Since the angle of incidence is unchanged, the reflection, CE, from the liquid surface is parallel to the reflection, BD, previously obtained from the metal surface. The distance between the two reflected beams can be measured, and is equal to the distance BC. The distance BC is the hypotenuse of a right triangle whose acute angles are 45° . One side of this triangle is perpendicular to the metal surface at B and is equal in length to the thickness of the film. The latter dimension can, therefore, be accurately computed by multiplying the measured distance, BC, by the cosine 45° or 0.707. If an angle of incidence other than 45° is used, the calculations of the film thickness become more complicated. If the angle of incidence of the beam varies 1° from the desired angle of 45° an error of about 2 per cent is made.

Arrangement of Apparatus

The instruments necessary for providing the light beam are relatively simple (Figure 2). Any light system that will project a sharply defined narrow (about 0.05 mm. wide)

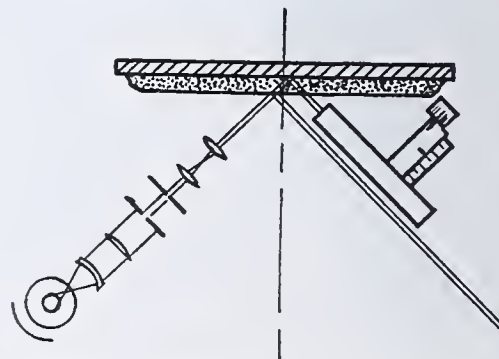


FIGURE 2. ARRANGEMENT OF APPARATUS

parallel beam easily visible under the conditions of general lighting is adequate. A satisfactory beam may be obtained by projection of light through two parallel slits. Sharp definition of the edges of the beam on the reflecting surface

may be made by use of appropriate focusing condensers. A common reference point in the intercepted beam can be established by insertion of a fine cross hair in the slit nearest the reflecting surface.

A micrometer microscope (Gaertner) comparator is a convenient instrument for making film thickness determinations. The essential parts of the instrument are a low-power microscope (2 cm. focal length) containing cross hairs for accurate sighting, a lateral slide to carry the microscope, and a micrometer screw provided with scale and vernier calibrated to 0.005 mm.

The projector and microscope should be mounted with their center lines in the same plane, and with the line bisecting the angle of their intersection perpendicular to the surface upon which measurements are to be made. When the surface is in a true vertical position, the center lines of the projector and microscope are in a horizontal plane and form an angle of 90° . This relation should be maintained for all measurements. The instruments, therefore, may be mounted in a fixed position on a common frame or base plate to avoid the necessity for repeated alignment. The angle of incidence of the projected beam of light may be conveniently adjusted with the aid of a 45° triangle. The beam can be aligned to parallel the hypotenuse edge of the triangle appropriately held against the surface upon which measurements are to be made. Accuracy of the adjustment may be verified by proper use of mechanics squares.

The construction of the comparator used in these studies is such that the microscope is perpendicular to the lateral slide plate. Consequently, a comparator of this type may also be conveniently aligned with the aid of a 45° triangle. A photograph of the assembly of the instruments is given in Figure 3.

It is essential, for accurate measurements, that the film be established upon a rigid and truly plane surface. For this, a 0.63-cm. (0.25-inch) thick steel channel, planed smooth on its flat surface, was used. The end of the planed steel was further machined to provide a perfectly straightedge over which milk, from an attached trough, could be evenly distributed. A straight-edge type of distributor (spillway type) was chosen because it permits free and natural formation of a film with small consequent effect on its initial velocity. Further to facilitate the study of the influence of gravity on the thickness of a film, a quiet smooth approach of the liquid to the distributor edge was obtained by use of a deep trough. The supply of milk to the trough was maintained at a predetermined rate by means of a float control.

Controlled flowing films deliver a definite quantity of liquid per unit time; consequently they have a definite capacity per unit width. Film capacity may be expressed in any convenient standard, such as pounds per lineal foot per hour. Physical characteristics of a film, such as velocity and thickness, adjust themselves to, and are dependent upon, the film capacity.

TABLE I. THICKNESS OF FILMS OF MILK

Flow Rate Lb./ft./hr.	Thickness of Film		
	Micrometer Mm.	Light beam method Mm.	Calculated from weight of film adhering on a metal strip Mm.
100	0.29	0.26
300	0.42	0.39
600	0.52	0.49
Nearly zero		0.0245	0.0238

A convenient procedure in determining the thickness of a film with the instrument assembly when properly aligned is by first establishing the desired film capacity over the flow surface area. By means of a short baffle placed on the distributor edge, the flow may be temporarily diverted from a narrow vertical area which includes the point at which a measurement is to be made, and where the narrow beam of light is being reflected. It is necessary to clean the area at the point of measurement by means of a dry cloth to assure reflection from the metal surface. The relative position of a line shadow in the reflected beam of light (shadow caused by cross hair inserted in the projector slit) can be determined by reading from the operative vernier and scale when the microscope is properly aligned. The flow may then be promptly restored by removal of the diverting baffle, and the changed position of the beam, now reflected from the surface of the

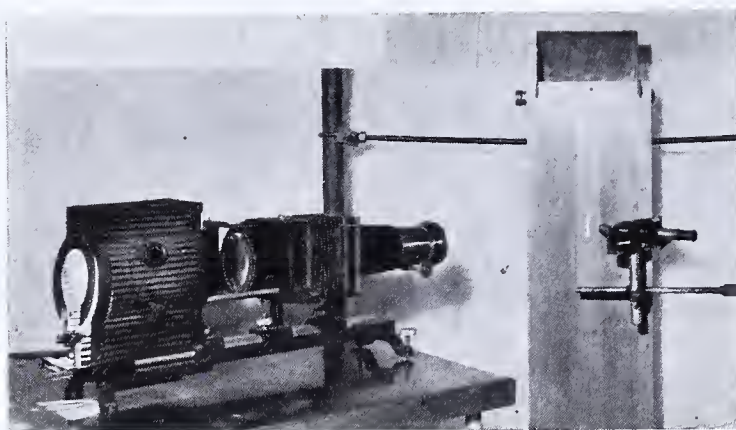


FIGURE 3. ASSEMBLY OF APPARATUS

film, read from the vernier scale. The difference of the two readings in millimeters is the distance DE or BC indicated in Figure 1, which when multiplied by $\cos 45^\circ$ gives the thickness of the film at the point of measurement. The stability of the apparatus during the interval of measurement may be determined by repeating the initial measurement when the flow of the fluid is again diverted by the baffle.

A number of measurements were made at the same points on several films by both the light beam and micrometer methods. The individual results by each method were averaged for the comparison presented in Table I. It will be observed that the measurements made with the light beam are less than those made with the micrometer. A further comparison was made by measuring and weighing a film adhering to a strip of metal and calculating the thickness from the weight of the film. These results are also presented in Table I.

Conclusions

A new method, employing reflected beams of light to determine the thickness of flowing films, is described. This method is sufficiently sensitive to detect variations in the thickness of a film, such as those caused by changes in the velocity, within successive short intervals.

Acknowledgment

The authors are indebted to H. C. Jackson of the Department of Dairy Industry and L. R. Ingersol of the Department of Physics of the University of Wisconsin, and the Wisconsin Alumni Research Foundation, for their considerate assistance and aid in providing facilities and apparatus for this work.

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Preparation of Diphenylamine Indicator Solution

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THE usual preparation of diphenylamine indicator by shaking the amine with concentrated sulfuric acid is slow and time-consuming. If the amine is first melted to a clear liquid (m. p. = 52.9°C.) and the required amount of concentrated sulfuric acid then added, complete solution may be effected by 15 to 30 seconds' shaking.

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Quantitative Determination of the Concentration of Vaporized Carbon Tetrachloride

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IN THE course of investigation of several research problems dealing with low molecular weight alkyl halides of the paraffin series, it became necessary to make a large number of determinations of the concentrations of vapors of these compounds in air. The problem of analyzing such air-halogenated hydrocarbon mixtures is not new and has been dealt with in various ways in numerous chemical and toxicological studies.

Fieldner, Katz, Kinney, and Longfellow (2) found the concentration of vaporized carbon tetrachloride in air by drying the sample over calcium chloride and soda lime, absorbing the organic vapor with weighed activated charcoal, and finding the increase in weight, making suitable deductions for the presence of inorganic halogen compounds. Robbins and Lamson (6) used an apparatus developed by Palmer and Weaver (4) for the determination of carbon tetrachloride in air, in which the resistances of two electrically heated wires, one surrounded by the gaseous unknown and the other by a reference gas, are compared. Nuckolls (3) found the concentration of carbon tetrachloride, chloroform, dichloroethylene, dichlorodifluoromethane, dichlorotetrafluoroethane, ethyl bromide, ethyl chloride, methyl bromide, methyl chloride, methylene chloride, and monofluorotrichloromethane, respectively, in air by means of a modified Burrell apparatus. "The apparatus consisted essentially of a liquefaction bulb having a side arm connected to a mercury manometer. The inlet of the bulb was provided with a three-way stopcock which connected on one side to a vacuum pump and on the other side to a U-tube, one arm of which was provided with a connection to the sampling tubes." The water vapor was removed by contact with anhydrous magnesium perchlorate and the sample of halogenated hydrocarbon was frozen with liquid air in the bulb from which the air was then removed by means of a vacuum pump. After returning the bulb to the original temperature, observation of the pressure exerted by the alkyl halide in a mercury manometer and the atmospheric pressure made it possible to calculate the concentration of the halogenated hydrocarbon in the sample.

None of the determinations described seemed suitable to the authors' purpose, as they were interested in a simple, specific chemical method which could be employed for large as well as small gas samples. Therefore, another method was developed, somewhat similar to that used by Robbins in determinations of carbon tetrachloride in animal tissues (5).

Principle of the Method

The method is based upon the observation that carbon tetrachloride vapor mixed with moist air is decomposed quantitatively into hydrogen chloride when passed through a silica tube heated to 1000° to 1100° C. By absorption and determination of the hydrogen chloride the concentration of the carbon tetrachloride vapor can be calculated. If water vapor is not present in sufficient amount, small amounts of chlorine are produced.

The accuracy of the method was checked by the determinations of known amounts of carbon tetrachloride vapor. The apparatus used is shown in Figure 1. The silica tube was heated by means of the electrical furnace, the temperature being controlled by means of the rheostat and measured by the thermocouple. The gases were drawn through the train by means of a calibrated water-filled aspirator of 18 liters in capacity. When it was necessary to measure larger volumes

of gas, an electrically driven suction pump was used and the volume measured by means of a gas meter. The various reagents used to absorb the hydrogen chloride are given in the tables.

Experimental Work

SET I. A very satisfactory method was devised to introduce accurately weighed samples of carbon tetrachloride into a stream of air.

The tip of an ordinary glass Gooch funnel (Figure 1) was sealed and a narrow arbitrary scale from 1 to 10 was attached along the length of the stem. The funnel was provided with a shellac-covered 2-hole cork stopper through which two right-angular glass tubes had been fitted. The inlet tube was long and drawn to a capillary which reached down to the stem of the Gooch funnel. The outlet tube was short and led to the hot silica tube. Before each run the Gooch funnel was closed with a solid shellac-covered cork stopper and weighed. Then 0.5 ml. of carbon tetrachloride was placed in the stem of the funnel, which was closed with the solid cork stopper and weighed again, thus giving the weight of the carbon tetrachloride used. A wire hook had been fastened around the modified Gooch funnel so that it could be suspended in a balance for weighing purposes. The arbitrary scale had been chosen so that 0.5 ml. of carbon tetrachloride reached approximately up to the 10 mark. Just before starting the run, the solid cork stopper was quickly replaced with the 2-hole stopper mentioned above.

A porcelain boat was filled with water and placed in the silica tube, as shown in Figure 1, in order to provide sufficient hydrogen for the formation of hydrogen chloride. In making the run a stream of uncontaminated air was sucked at a definite rate through this carbon tetrachloride vaporizer into the heated silica tube and the reagent bottles. The volatilization of the carbon tetrachloride into the air was kept as constant as possible by slightly raising or lowering the inlet tube within the vaporizer. The internal diameter of the combustion tube was 1.56 cm. (0.625 inch). It is important to mount the constricted end of the tube as close to the furnace as possible without burning the rubber tube joint to prevent moisture from condensing in the cold end, which would hold hydrogen chloride in solution.

SET II. The experiments in set II were conducted in an especially constructed experimental room having a volume of approximately 32 cubic meters. The walls and floor of the room were concrete and the ceiling was "transite" asbestos board. The room had five steel casement windows, 70 × 100 cm., four opening to the outside and one to the adjacent analytical laboratory, and a door in the end of the laboratory wall. The entire inside of the experimental room had been given two coats of sodium silicate, brushed with dilute hydrochloric acid, and finally sprayed with two coats of a Bakelite varnish. Each covering was allowed to dry thoroughly before a new layer was applied to the wall.

Two linen towels were suspended in this room and wetted with a measured volume of carbon tetrachloride, taking care that no liquid carbon tetrachloride dropped from the towels onto the floor. Then a powerful fan was turned on in the experimental room for 10 to 15 minutes in order to volatilize the carbon tetrachloride and render the atmosphere in the room as uniform as possible. Afterwards, air was drawn from this experimental room through a glass tube located at the 150-cm. (5-foot) level directly into the hot silica tube in the test room and thence into the gas-washing bottles.

SET III. In connection with experimental work on the physiological effect of carbon tetrachloride vapor, it was desired to modify the method of determination so that it was suitable for low concentrations, and could thus be used

TABLE I. EXPERIMENTAL CONDITIONS AND RESULTS OF TESTS IN SET I

(Using known amounts of carbon tetrachloride vapors in air)

No.	CCl ₄ Used Mg.	Temp. of Furnace ° C.	Rate L./min.	Vol- ume of Sample Liters	CCl ₄ Found in Each Gas-Washing Bottle					CCl ₄ Found		CCl ₄ in Air by Volume	
					1	2	3	4	5	Mg.	%	Used %	Found %
2	765.1	993	0.5	10	91.4 ^a	3.8 ^a	1.9 ^a	1.7 ^b	0.0	755.9	98.8	1.20	1.19
3	765.1	1038	0.5	10	79.5 ^c	2.3 ^c	1.3 ^c	1.3 ^b	0.0 ^d	645.8	84.4	1.20	1.01
4	741.5	1017	0.5	9.75	84.0 ^e	4.8 ^e	2.9 ^e	1.5 ^e	2.6 ^f	710.4	95.8	1.19	1.14
5	774.2	1040	0.33	8.33	85.6 ^e	5.4 ^e	2.8 ^f	1.3 ^c	1.5 ^f	747.9	96.6	1.45	1.40

Reagents used:

^a 50 ml. of 1 N aqueous sodium hydroxide.

^b 50 ml. of 95 per cent ethyl alcohol.

^c 50 ml. of 1 N alcoholic sodium hydroxide.

^d 50 ml. of paraffin oil (used in order to absorb chlorides or undecomposed carbon tetrachloride, if present).

^e 50 ml. of 2 N aqueous sodium hydroxide.

^f 50 ml. of 10 N aqueous sodium hydroxide.

TABLE II. EXPERIMENTAL CONDITIONS AND RESULTS OF TESTS IN SET II

(Using carbon tetrachloride-air mixtures in experimental room of 32 cu. meters (1130 cu. feet) capacity)

No.	CCl ₄ Used Grams	Tem- perature of Furnace ° C.	Time of Sampling Min.	Volume of Sample Liters	CCl ₄ Found in Each Sampling Bottle ^a			CCl ₄ Found		Concentration of CCl ₄ in Room	
					1	2	3	%	Grams	Used P. p. m.	Found P. p. m.
1	50.7	1100	65	18	97.0	0.0	0.0	97.0	49.2	250	243
2	50.7	1100	72	18	95.6	0.0	0.0	95.6	48.2	250	239
3	101.4	1100	72	18	93.7	0.0	0.0	93.7	95.0	500	469
4	101.4	1100	72	18	95.1	0.0	0.0	95.1	96.4	500	476

Av. 95.4

^a Three gas-washing bottles were used in series, each bottle containing 50 ml. of 10 N aqueous sodium hydroxide.

Rate, 0.5 liter per minute.

as a check on the calibration of more indirect but more rapid methods for estimation.

To increase the efficiency of the method slightly, the silica tube was packed with 10-mm. lengths of 5-mm. quartz tubing. The total packed length of the quartz combustion tube was 35 cm. (14 inches) with a 30-cm. (12-inch) furnace. Enough of the small packing tubes were used to fill the space, and were held in place with loose plugs of ignited asbestos fiber, about 2.5 cm. (1 inch) of plug at each end. After packing the tube, the free flow of air through the tube was tested by gently blowing through one end. It is important to make this simple test, as the asbestos is easily packed too tightly. The chloride absorbed was determined by titration with standard silver nitrate solution (1 ml. = 1 mg. of carbon tetrachloride) using potassium chromate as indicator and working in a darkroom in bright yellow light, as is done in water analyses (1). Otherwise, no change was made in the method for these trials. Nine trials were conducted, using air samples of 10 liters as measured by the aspirator bottle (actually close to 9 liters when corrected for pressure drop and water picked up in the aspirator).

For lower concentrations of carbon tetrachloride it was desirable to decrease the volume of absorbing fluid to avoid the need for inconveniently large air samples. It was found possible to absorb the hydrogen chloride formed in the silica tube in 50 ml. of 2 N sodium hydroxide with the same accuracy as in the five absorbing bottles of the original method, if a fritted glass (Jena) distributing disk was used for the production of fine bubbles, and if 5 ml. of ethyl alcohol or 0.5 ml. of 0.1 per cent saponin were added to reduce bubble size. The determination was carried out as before, save that the sodium hydroxide and washings were made up to only 100 ml.

For the measurement of smaller amounts of carbon tetrachloride (1 mg.) with accuracy equivalent to that when weighing 10 mg., a capillary buret similar to that described by Smyth (2) was employed, 1 mm. on the capillary corresponding to 0.22 mg. of carbon tetrachloride, and estimates to 0.02 mg. being possible without a reading telescope. In all trials at concentrations below 100 p. p. m., a buret graduated in 0.02 ml. was used for the titration.

As a preliminary to contemplated work on the determination of carbon tetrachloride by automatic means employing a recording conductivity bridge, tests were made of the efficiency of absorption of the hydrogen chloride formed in distilled water. Fifty milliliters of water in a fritted glass gas wash-

ing bottle were used. The acid absorbed was titrated with sodium hydroxide, 1 ml. of which is equivalent to 1.9235 mg. of carbon tetrachloride. Bromothymol blue was used as the indicator, carrying the titration to a pH of 7. Some error must have been introduced by the carbon dioxide formed in the silica tube, but in view of the results obtained it is judged to be low. Since no formation of free chlorine in the silica tube was desired, tests were made with preliminary humidification of the air before it entered the tube, but after it picked up the carbon tetrachloride.

SET IV. The tests outlined in set II were repeated using the improved method described in set IV. The changes made included packing the silica tube with a large number of 5-mm. lengths of 5-mm. quartz tubing held in place by loose plugs of ignited asbestos fiber, the use of a gas-washing bottle provided with a fritted glass (Jena) distributing disk 20 mm. in diameter, and the addition of 5 ml. of ethyl alcohol to 50 ml. of 2 N sodium hydroxide.

Titration Procedure

At the end of the sampling, some additional pure air was drawn through the apparatus in order to flush out any residual vapors. As soon as the run was completed the contents of each absorption bottle containing alcoholic or aqueous sodium hydroxide were transferred to a 100- or 200-ml. volumetric

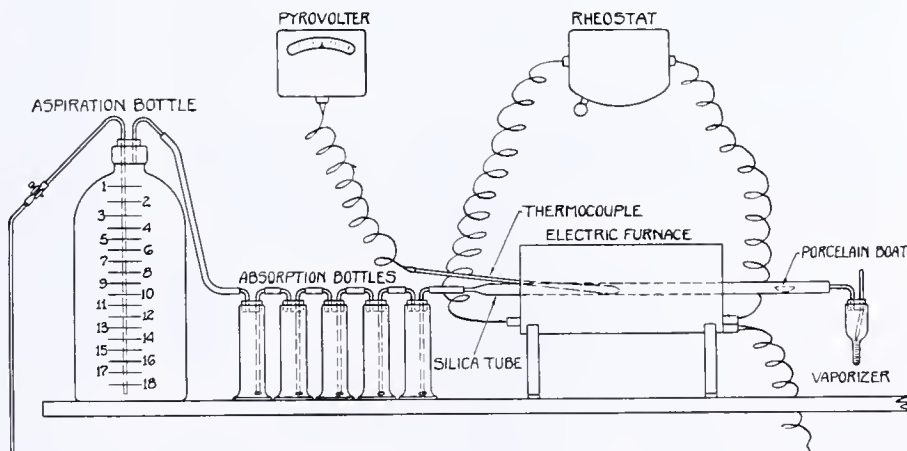


FIGURE 1

TABLE III. EXPERIMENTAL CONDITIONS AND RESULTS OF TESTS IN SET III

(Using the improved method of determination of known amounts of carbon tetrachloride vapors in air)

Special Conditions	Test No.	CCl ₄ Used	CCl ₄ in Air	CCl ₄ by Volume	CCl ₄ Found	
		Mg.	Mg./l.	P. p. m.	Mg.	%
Standard, save silica tube packed	48	19.4	2.2	350	19.2	99.0
	47	20.7	2.4	380	20.6	99.5
	24	51.8	5.7	910	50.9	98.3
	29	55.7	6.3	1000	55.5	99.6
	37	64.7	7.2	1150	63.3	97.8
	28	75.2	8.4	1340	73.4	97.6
	30	140.1	15.9	2530	137.5	98.1
	45	180.2	20.2	3200	177.8	98.7
	46	425.4	47.8	7600	420.6	98.9
					Av.	98.4
Tube packed, HCl absorbed in 50 ml. of 2 N NaOH + saponin	88	51.2	5.6	890	49.9	97.5
	91	55.1	6.0	950	54.0	98.0
	97	58.5	6.4	1020	57.7	98.3
	99	74.5	8.2	1300	73.8	99.1
	98	98.4	10.8	1720	95.7	97.3
					Av.	98.0
Tube packed, HCl absorbed in 50 ml. of 2 N NaOH + ethyl alcohol	95	49.1	5.3	840	48.0	97.8
	82	64.5	7.1	1130	63.5	98.4
	81	116.3	12.8	2040	114.5	98.4
					Av.	98.2
Tube packed, CCl ₄ measured by volume, absorbed in 50 ml. of 2 N NaOH + saponin	109	1.03	0.11	18	1.01	98.0
	110	1.80	0.20	32	1.81	100.6
	108	3.59	0.39	62	3.62	100.8
	107	11.68	1.27	202	11.50	98.5
					Av.	99.5
Tube packed, CCl ₄ by volume, absorbed in 9 ml. of NaOH in spiral	111	0.58	0.063	10	0.58	100.0
	112	3.60	0.39	62	3.54	98.3
					Av.	99.2
Tube packed, absorbed in water: Sample 0% humidity	124	52.5	5.6	890	21.0	40.0
	123	100.6	10.7	1700	43.9	43.8
					Av.	41.9
Sample 70% humidity	134	43.4	4.6	730	42.1	99.3
					Av.	99.3
Sample 100% humidity	128	32.8	3.6	570	31.8	97.0
	130	42.4	4.6	730	42.1	99.3
	127	50.6	5.6	890	50.2	99.2
	122	52.3	5.7	910	50.5	96.5
	120	55.4	6.1	970	52.6	95.0
	125	57.0	6.3	1000	56.1	98.4
	126	64.4	7.1	1130	63.9	99.2
	121	73.3	8.1	1290	72.4	98.8
	119	98.0	10.7	1700	97.8	99.8
	129	138.0	14.8	2360	136.4	98.8
					Av.	98.2

flask and diluted to the mark. Several samples were pipetted out and two different analyses were made. Since all the carbon tetrachloride was to be titrated as sodium chloride, when tests showed some of the chlorine formed during the thermal decomposition was present in the solution in the form of sodium hypochlorite, it became necessary to convert the sodium hypochlorite to sodium chloride. This reduction was brought about by the addition of 0.1 N sodium sulfite. However, in order to ensure the addition of a sufficient amount of this reducing agent, it became necessary to conduct a preliminary analysis for the purpose of determining the sodium hypochlorite concentration of the solution. This is unnecessary when it is certain that the relative humidity of the air sample approaches 100 per cent, since in this case no hypochlorite is formed during absorption.

PRELIMINARY ANALYSIS. The test portion was treated with 10 per cent potassium iodide and acidified with dilute hydrochloric acid. The iodine liberated by the interaction between the potassium iodide and the sodium hypochlorite was titrated against 0.1 N sodium thiosulfate, using starch as indicator.

PRINCIPAL ANALYSIS. As the volume of 0.1 N sodium thiosulfate used in the preliminary analysis was a direct measure of the sodium hypochlorite concentration of the solution, this volume was taken as an indication of the proper amount of 0.1 N sodium sulfite to be added to the sample. Actually, the amount of 0.1 N sodium sulfite added exceeded the volume of 0.1 N sodium thiosulfate used by 10 per cent. The solutions taken for analysis were treated with the proper amount of 0.1 N sodium sulfite and a few drops of phenolphthalein; enough dilute nitric acid was added to make the solution only faintly alkaline to phenolphthalein. The samples were allowed to cool to room temperature, 2 ml. of 1 M sodium bicarbonate were added, and the solutions were made just faintly alkaline to litmus with dilute nitric acid. Then 2 drops of 10 per cent potassium chromate were added as indicator and the solutions were titrated with standard silver nitrate, using yellow artificial light and excluding daylight.

In the case of the nonalkaline reagents some aqueous sodium hydroxide was added at the end of the run and the analysis was conducted as given above.

Suitable blanks were run in every case and proper deductions were made to account for chlorides present in the reagents and the atmosphere.

Experimental Results and Conclusions

Tables I to IV give the conditions and data in the four sets of experiments described above, and clearly indicate that this method is well adapted for the determination of the concentration of vaporized carbon tetrachloride in air.

In carrying out the determination given in Table I, various absorbing reagents for the hydrogen chloride were tried. As even the fifth bottle showed appreciable amounts of chloride, it is obvious that absorption was not complete with the type of absorption vessel and procedure used.

The results given in Table III showed an average of 98.6 per cent of the carbon tetrachloride accounted for, with concentrations from 350 to 7600 parts per million by volume. Varying the sampling rate from 250 to 1000 ml. per minute did not affect the accuracy of the method.

Five trials at concentrations between 890 and 1720 p. p. m. with saponin averaged 99.1 per cent recovery and three with alcohol 98.2 per cent recovery, as indicated in Table III.

When using the capillary buret, previously described, samples of 10 liters of air with carbon tetrachloride concentrations ranging from 18 to 202 p. p. m. gave recoveries averaging 99.5 per cent when saponin was used in 50 ml. of sodium hydroxide. Similar trials where the hydrogen chloride formed was absorbed by 9 cc. of sodium hydroxide in a spiral absorber similar to that described by Smyth (7) gave recoveries averaging 99.1 per cent for concentrations of 10 to 62 p. p. m. It is believed that 10 p. p. m. is not the lower limit of accuracy of the method, although no present need required trials with lower concentrations.

Using water as absorbent, it was shown that 70 per cent humidity (obtained by bubbling the air sample through 10 N sodium hydroxide) prevented the formation of chlorine, and data reported in Table III show that at this humidity determination of hydrogen chloride by absorption in water is accurate. Ten trials with 100 per cent humidity (obtained by bubbling the air sample through water) showed recoveries averaging 98.2 per cent with concentrations between 570 and 2360 p. p. m., just as good as when the hydrogen chloride was absorbed in sodium hydroxide.

TABLE IV. EXPERIMENTAL CONDITIONS AND RESULTS OF TESTS IN SET IV

(Using carbon tetrachloride-air mixtures in experimental room of 1130 cubic feet capacity and utilizing the improved method of determination)

No.	CCl ₄ Used Grams	Temperature of Furnace ° C.	Time of Sampling Min.	Volume of Sample Liters	CCl ₄ Found in Each Sampling Bottle ^a		CCl ₄ Found		Concentration of CCl ₄ in Room	
					1	2	%	Grams	Used	Found
					%	%	%		P. p. m.	P. p. m.
1	101.4	1100	72	18	97.2	0.0	97.2	98.6	500	486
2	101.4	1100	72	18	97.7	0.0	97.7	99.1	500	489
3	101.4	1100	72	18	96.5	0.0	96.5	97.8	500	483
4	50.7	1100	72	18	97.0	0.0	97.0	49.2	250	243

^a The first absorption bottle contained a fritted disk, while the second was of the ordinary type.

The experiments outlined in Table IV again indicate the quality of the results obtained with the improved method in the experimental room. However, experiments carried out in such a test room can yield good results only if (1) the atmosphere is uniformly mixed, (2) the test room is sufficiently tight so that there will be no appreciable flow of atmosphere from the test room to the outside, or vice versa, during the course of the test, and (3) the surface of the interior of the test room does not react with any constituent of the atmosphere to be tested. The experiments can become highly unsatisfactory if any of these conditions is not fully satisfied.

The thermal decomposition method with the slight modifications given accounts for at least 97.3 per cent of carbon tetrachloride vapor present in air, down to a concentration of 10 p. p. m., and probably lower. Since absorption in distilled water will give recoveries of almost this degree, the method is suitable for development of continuous automatic indicating equipment based on electrical conductivity. It is believed that the chemical method described, as well as the

electrical method suggested, is generally applicable to the quantitative determination of vaporized halogenated hydrocarbons other than carbon tetrachloride in air. It is planned to conduct further tests in this field in order to confirm this conclusion.

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Determining the Resistance of Portland Cement to Sulfate Waters

An Accelerated Test

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DURING the past few years many investigations have been made on the resistance of Portland cement concrete to corrosive salt waters. The conclusions regarding the actively corrosive constituent therein have almost invariably been that the sulfate ion is primarily responsible for the reactions leading to the eventual disintegration of the concrete. It is likewise now generally agreed that even the most dense practical combinations of aggregates and cement will not surely resist the corrosive action of highly sulfated natural waters. It is only by the use of a cement which does not readily react with sulfates that long life of an exposed concrete structure is to be expected.

The preponderance of experimental evidence indicates that, if the cement is made under conditions obtaining in the best modern practice of manufacture, its resistance to sulfate action can be reasonably well deduced from its chemical composition. The method is to compute the hypothetical compound composition from the results of the usual chemical analysis, as proposed by Bogue (1), and then from the percentage of the sulfate-sensitive compounds to estimate its probable resistance. The tricalcium aluminate is widely regarded as the source of all evil in the family of cement compounds in most of those properties which tend to make concrete less durable, and indeed its properties—i. e., those of the pure compound—fully warrant these suspicions. Therefore the present practice in consumer specifications, when a high sulfate-resistance is desired, is to specify a composition which will make the percentage of this compound as low as

The present active interest in the manufacture of Portland cements which will produce concretes highly resistant to the action of natural waters has created a need for a reliable but short-time laboratory test to determine this resistance. The slab-warping test herein proposed is believed to give a reliable indication of the probable resistance of the cement to sulfate-bearing waters, and compares favorably with long-time tests of concrete cylinders made from the same cement. It has the merit of being completed within 28 days, so that it is suitable for acceptance test purposes.

is economically feasible. A number of specifications have recently been written with a restriction of this nature, notably those of the Metropolitan Water District of Southern California (5), and of the Bureau of Reclamation (3), and the results of tests have shown that this procedure has been reasonably well justified. Nevertheless, it is not to be presumed that a similar sulfate-resistance-compound-composition relationship will necessarily hold for other geographical areas where the raw materials and manufacturing practice

may be somewhat different. Therefore it is desirable to have a reliable short-time test which will directly measure the sulfate-resistance of a cement and whose results will be available by the time the usual 28-day strength tests are completed. One such test has been incorporated in the specifications (7) for the Fort Peck Dam, Montana, but no data regarding the results of its use and comparison with actual concrete tests have been published.

The slab-warping test which is here described has been applied to Portland cements having a wide variation in chemical composition, and has been found to give a good correlation with long-time compressive strengths of the corresponding mortar and concrete cylinders. Since it is fundamentally an expansion test, it must be used with caution on cements other than the Portland variety, such as cements with pozzuolanic admixtures, and it is not applicable to high-alumina cements in which sulfate disintegration may proceed without external volume changes.

The test consists in casting a neat-cement specimen 5 X

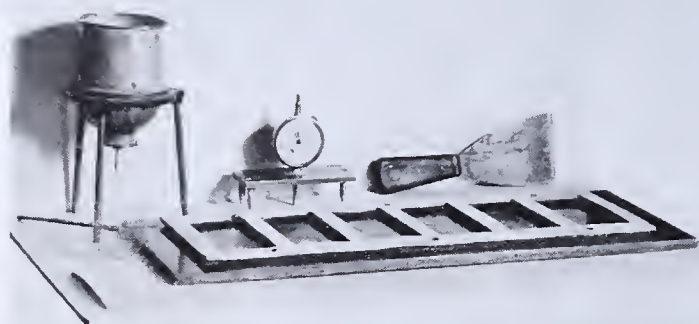


FIGURE 1. APPARATUS ENSEMBLE FOR MOLDING CEMENT SLABS

11.25 × 0.32 cm. (2 × 4.5 × 0.125 inch) from a sample of the cement to be tested, using a water-cement ratio of 0.40 for most cements. After the cement has obtained its final set, the top surface is scraped and the specimen immersed in water for 7 days. It is then coated with an impervious material on the bottom, and immersed in a 10 per cent solution of sodium sulfate. Because of attack (and therefore expansion) on only one face, the specimen will tend to warp, the extent of the warping being used as an indication of the extent of the attack.

Figure 1 shows the apparatus used in preparing the specimens, consisting principally of a gang brass mold, a rubber gasket for increasing the depth of the specimens, a mixing cup, and a spherometer. Figure 2 shows in more detail the spherometer used for measuring the extent of the warping in the slabs.

Procedure

The brass mold is first prepared by coating it with a thin layer of oil, such as a mixture of paraffin and motor oil, to prevent adhesion of the specimen to the form, and the rubber gasket is cemented on the mold with rubber cement. For each slab to be prepared, 100 grams of cement are weighed out and mixed with distilled water (from a pipet) to give the required water-cement ratio. This ratio is standardized at 0.40 by weight for a cement having a normal consistency of 22.5 per cent. If the normal consistency of the cement to be tested is greater or less than this by more than one unit, then for each unit greater than 23.5 or less than 21.5 the water-cement ratio is increased or decreased by 0.005 unit, respectively.

The water and cement, which should be within 5° of 21° C. (70° F.), are mixed preferably in a round-bottomed cup which has an opening in the bottom from which the cement paste may be drawn while it is still being stirred. The stirring should be done in such a manner that no air is incorporated during the process, and should have a duration of about 2 minutes after initial mixing. At the end of this time, if the mixture is entirely homogeneous, the paste is allowed to flow into the mold, the stirring being continued until the form has been filled to the top of the rubber gasket. The paste is spread evenly in the form with a spatula, using a slight tapping on the bottom to facilitate escape of any entrained air bubbles. Any excess paste is struck from the surface with the spatula, and the adjacent form is then filled in a similar manner with the next mixture. Unless these operations are performed in a moist room, they should be done as rapidly as possible to avoid any evaporation during the process.

As soon as the preparation of the specimen is completed, the mold is placed in a moist room at 21° C. (70° F.) and protected

with wet cloths to prevent any water's dripping upon the surface. After storage for 16 to 20 hours, the rubber gasket is removed and the specimens are carefully scraped with a stiff steel spatula until their surfaces are level with that of the brass mold. The last few scrapings should be done with special care to avoid any gouging or other impairment of the surface, and are usually best done by drawing the spatula in a vertical position toward the operator. There should be no pressure of the flat part of the blade against the surface, such manipulation having the effect of glazing it and therefore introducing a possible variation.

Immediately after scraping, the mold and slabs are placed in a covered pan of fresh distilled water and allowed to cure in this way for 3 days. At the end of that period the mold is stripped from the slabs, which are replaced in the water.

On the seventh day the slabs are removed, and the bottom surface (unscraped surface) and sides are quickly dried with a towel and then painted with a coat of adherent waterproof paint, such as Goodrich acid seal primer No. 8. The top surface must never be allowed to become dry and the process should be carried out as expeditiously as possible. The slabs are then placed face

down upon a wet cloth in the moist room (protected from water spray) for about 2 hours. Any moisture is then quickly wiped from the painted side and a brush coat of hot beeswax and paraffin (50-50) is applied. They are replaced in the pan of water for at least 15 minutes, then removed and marked with the template to define the position of the spherometer legs.

The initial spherometer reading is then taken and recorded, and the slabs are placed in a 10 per cent sodium sulfate solution (100 grams of anhydrous salt per liter of water). Subsequent readings may be taken at periods of 3, 7, 13, 17, and 21 days after immersion, but the 7-day and 21-day readings at least must be obtained.

The susceptibility of the cement to attack by sulfate solution is indicated by the difference in the spherometer readings between the 21-day and the 7-day period.

With each group of slabs there should be made a control slab of a cement whose warping curve has been well established. If the

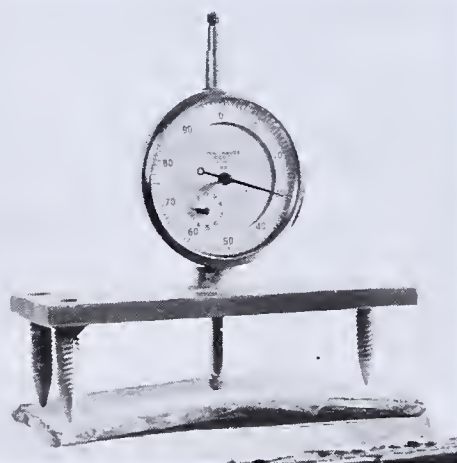


FIGURE 2. SPHEROMETER FOR MEASURING SLAB WARPING

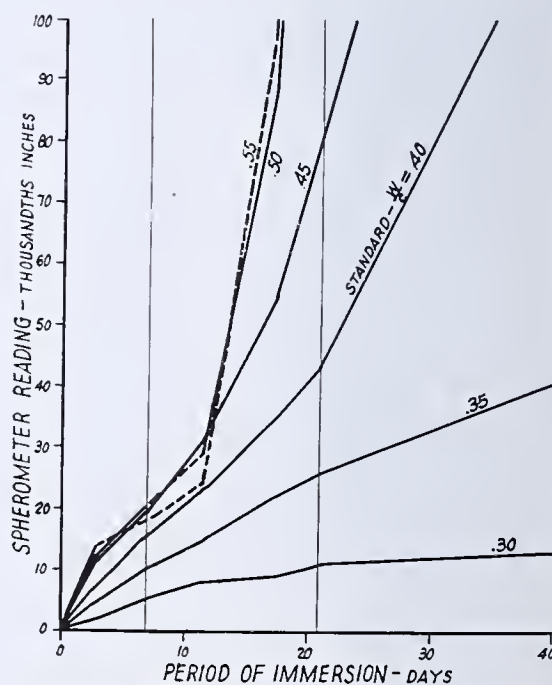


FIGURE 3. EFFECT OF WATER-CEMENT RATIO ON WARPING OF NEAT-CEMENT SLABS (D68 cement)

readings on this slab are out of line with its predetermined values, a faulty technic may be suspected and the test should be repeated.

The test is of course essentially an index of the amount of expansion produced in the cement by the sulfate attack.

From geometrical considerations it is easily seen that for

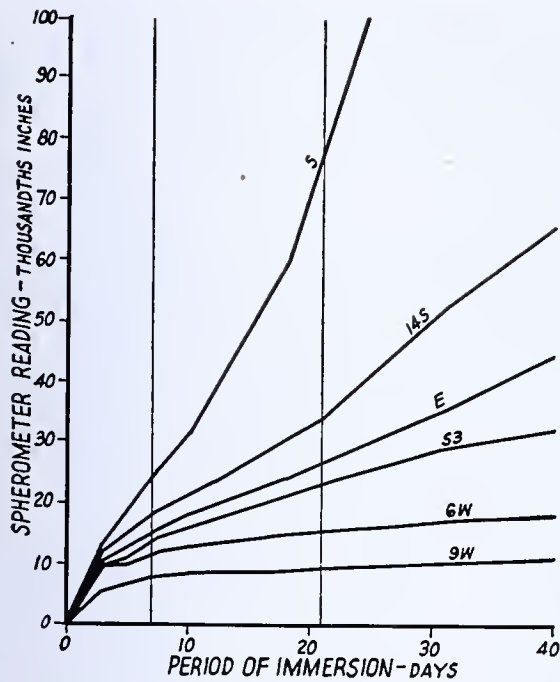


FIGURE 4. WARPING OF SLABS IN 10 PER CENT SODIUM SULFATE SOLUTION

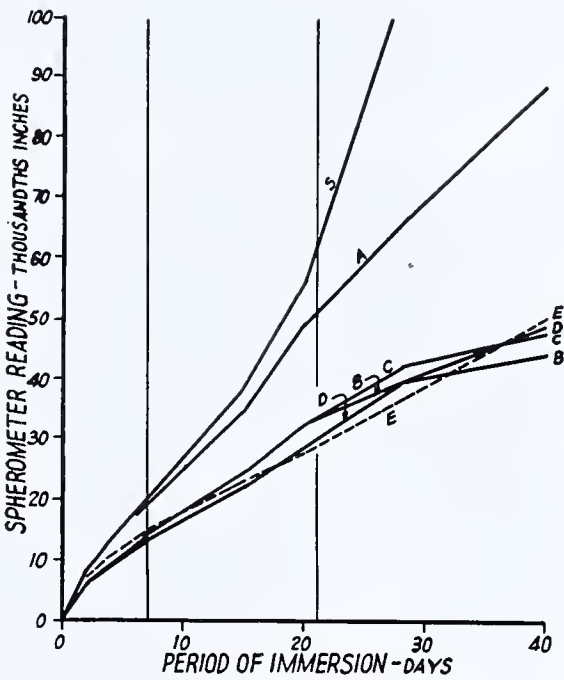


FIGURE 5. WARPING OF SLABS IN 10 PER CENT SODIUM SULFATE SOLUTION

small values the deflection is about four times as great as the expansion in the top fibers, thus magnifying the expansion effect.

The effect of the water-cement ratio on the degree of warping of the slabs is shown in Figure 3. The sensitivity of the test to this ratio is rather high, so that care must be exercised in the proportioning.

Test results on various types of cement in 10 per cent sodium sulfate are shown graphically in Figures 4, 5, and 6. Figure 7 shows comparable specimens in magnesium sulfate. The curves, which have been drawn through the observed points and are in no way idealized, indicate that the warping is a regular, continuous process, at least until large cracks begin to appear. In order to obtain a numerical value from the curves, the difference between the 21-day and the 7-day readings has arbitrarily been chosen as the slab-warping index to indicate the relative resistance of the specimens to sulfate attack.

The chemical composition of the cements tested is shown in Table I, in which are also given the 7- to 21-day index and the compressive strength index of 7.5×15 cm. (3×6 inch) concrete cylinders made from the same cement, after 6 months' exposure in 10 per cent sodium sulfate solution. This index is the per cent disintegration of the specimen measured by the ratio of the strength of the cylinders in the solution to those cured in a moist room for the same period, subtracted from unity. Thus 20 per cent disintegration indicates that the compressive strength of the sulfate-exposed cylinder is 80 per cent that of the corresponding moist cured specimen, at 6 months. In the case of the MWD specimens the slabs were not made from the same lot of cement, but from other lots from the same mill having a similar composition. The compounds are computed by the method of Bogue (1), no account being taken of any free lime present.

The last two columns of Table I show that with the exception of the "blended" cement E, the slab-warping index is

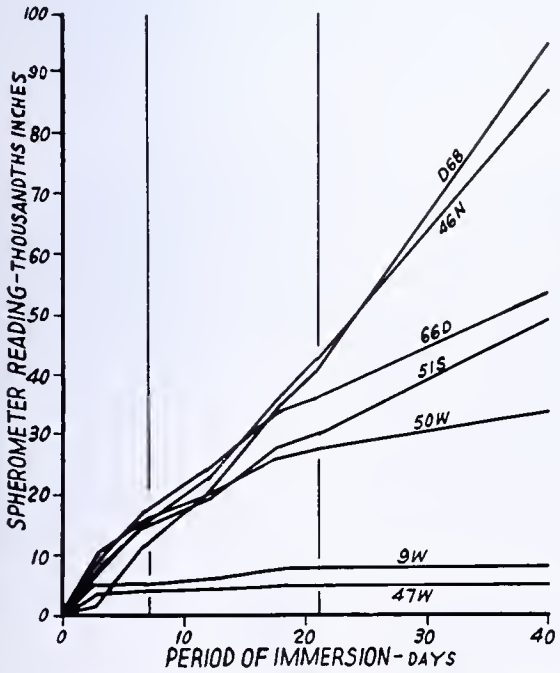


FIGURE 6. WARPING OF SLABS IN 10 PER CENT SODIUM SULFATE SOLUTION

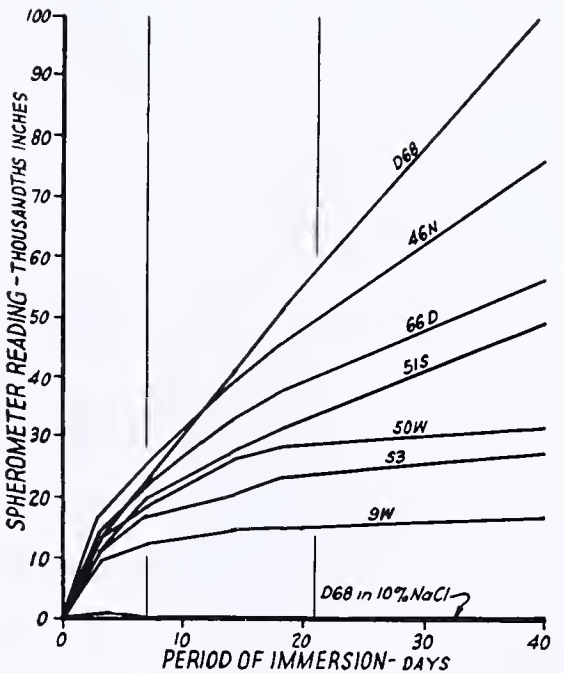


FIGURE 7. WARPING OF SLABS IN 10 PER CENT MAGNESIUM SULFATE SOLUTION

TABLE I. DISINTEGRATION OF CONCRETES AND NEAT CEMENTS IN 10 PER CENT SODIUM SULFATE SOLUTION

Cement No.	Type	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Fineness Sq. cm./g.	Compressive Strength Index; % Disintegration at Six Months	
							Slab-Warping Index	Slab-Warping Index
S	Commercial	49	23	10	7	1700	48	100
A	Laboratory	53	23	12	8	2200	32	100
D68	MWD specif. 68	51	22	10	8	1700	29	100
46N	MWD specif. 79	37	32	6	18	1950	26	92
B	Laboratory	60	15	8	13	2200	20	46
C	Laboratory	54	23	9	11	2200	20	52
66D	MWD specif. 79	52	21	6	13	1900	18	100
D	Laboratory	40	34	8	14	2200	17	33
14S	MWD specif. 79	46	26	6	13	2000	16	21
51S	MWD specif. 79	51	21	6	14	2000	15	50
E	Laboratory-blended	B with 20 per cent admixture				2200	11	0
50W	MWD specif. 79	52	29	7	5	1850	11	7
S3	Commercial sulfate resistant	60	13	2	16	1900	9	2
6W	MWD specif. 79	46	36	6	5	2000	4	0
9W	MWD sulfate resistant	39	46	4	5	2000	2	0
47W	MWD sulfate resistant	46	38	4	4	2000	1	0

TABLE II. COMPARISON OF SODIUM AND MAGNESIUM SULFATE ACTION

Cement	Warping Index	
	In 10% sodium sulfate	In 10% magnesium sulfate
D68	29	35
46N	26	24
66D	18	18
51S	15	13
50W	11	10
9W	2	4
47W	1	..

generally parallel to the compressive strength index, the displacements of 66D and 51S being due to the fact that cement from different lots of the same mill was used for these comparisons. It appears that cements with an index of 10 or less may be regarded as highly resistant to sulfate action, while those above 10 will be proportionately more susceptible.

A survey of the properties given in Table I indicates that no one compound can be held to be solely responsible for a lack of sulfate-resistance of the cement. In agreement with the results of other investigators (2, 4, 6), the sulfate-resistance is roughly inversely proportional to the tricalcium aluminate content, but it is evident that some of the other compounds and the fineness also exert an influence. It is interesting to note, for example, that cements 14S and 6W, which are similar except for percentage of the aluminoferrite compound, have considerably different sulfate-resistant characteristics, although the tricalcium aluminate content is the same for both. The higher tricalcium silicate contents also tend to make the cement less resistant and, as is to be expected, the coarser cements are somewhat inferior to the finer cements. More extended comparisons than these are, however, not warranted, since most of these cements were made in commercial mills, and a fine distinction in compound composition is an extrapolation to ideal equilibrium conditions which can hardly be expected to obtain in this case. Nevertheless, the general dependence of the cement resistance on chemical composition for products from several different sources tends to justify recent trends of specifying compound limits when sulfate-resistance is of primary consideration.

Resistance of cements to solutions other than sodium sulfate is also of interest, and Figure 7 shows the curves for a 10 per cent solution of magnesium sulfate. Table II compares the warping index for the two solutions; the values are

nearly the same and are definitely in the same relative order, which indicates that, at least so far as this test is concerned, the influence of the positive ion is of minor consequence in comparison to the activity of the sulfate ion. The curve for a 10 per cent solution of sodium chloride in Figure 7 shows the negligible effect of this salt upon the highly sulfate-susceptible D68 cement.

The degree of reproducibility of the test during the period of its use in this laboratory has been good. An indication of this is seen in the curve for cement D68 which appears in Figures 3 and 6, each of which represents a different slab made at different times, from the same sample of cement. The same is true for the curves of 9W in Figures 4 and 6, and for E in Figures 4 and 5. While the position of the curves on the ordinate scale sometimes varies from one test to another, the slopes themselves are usually constant, so that the warping index (which measures the slope) can be reasonably well reproduced. In this connection it has been found that long storage (a year or more) of a cement sample causes it to show markedly lower attack than originally. No tests have been made with concretes to find whether the aged cement would behave similarly in such a specimen, so that caution must be exercised in making the test on other than fresh cements.

The test has also been applied to natural soils which were suspected as potentially corrosive to concrete structures. The method was to saturate the soil with water, adding a little excess, and to immerse the slabs in the resulting mud. A soil having a sodium sulfate content of 380 p. p. m. showed only a slight attack, while one having 5000 p. p. m. showed a warping index of 19, using the susceptible cement D68.

There are, of course, many other applications in which the slab-warping test might prove fruitful, such as a study of the corrosivity of natural waters, of the effects of other salts and salt concentrations, and of the temperature influence on rate of attack.

Acknowledgment

This work represents a portion of the results of investigations conducted by the Metropolitan Water District of Southern California in connection with the construction of the Colorado River Aqueduct. The laboratory at Banning is under the direction of Lewis H. Tuthill, testing engineer, reporting in matters of investigation and research to Julian Hinds, assistant chief engineer. F. E. Weymouth is chief engineer and general manager. Acknowledgment is made to E. C. Reid and the laboratory staff at Banning for their generous coöperation.

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The Microestimation of Acetyl Groups

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THE importance of possessing a completely trustworthy method for estimation of acetyl groups is emphasized by the great value of acetylated derivatives in sugar chemistry and the significant role which recent biochemical investigations have ascribed to acetyl groupings in substances of biological interest. Especially is this so in the examination of substances of unknown constitution where the result of a determination must be used for the formulation of a reliable structure for the substance.

Almost all methods, including the one here described, involve a preliminary hydrolysis of the sample followed by a determination of the acetic acid liberated, either in the reaction mixture itself (which is possible only if the solution is not so colored as to obscure the transition of an indicator or where, if that condition prevails, the titration is performed electrometrically, 11), or subsequent to its removal therefrom by distillation. The methods of Freudenberg and his co-workers (2, 4), where transesterification in alcoholic solution and separation of the ethyl acetate formed precede saponification, and the method of Kuhn and Roth (6), where examination of the products of chromic acid oxidation is involved, are exceptional. A comprehensive review of the literature up to 1931 has been made by Meyer (8).

Since the appearance of the micromethod of Pregl and Soltys (10) who used *p*-toluene sulfonic acid as hydrolyzing agent, there have been two significant attempts to modify this technic in order to overcome certain inherent defects.

The first of these is the method of Friedrich and Rapoport (5) who essayed a simplification of the apparatus and the manipulation. The use of a small Claissen flask as hydrolyzing vessel and the omission of the U-tube make the apparatus simpler, and the replacement of the acidimetric titration by the more elegant iodometric method is a desirable improvement. However, the regulation of the air stream through the apparatus during the distillation *in vacuo* to so slow a rate (only one bubble in 1 to 2 seconds) is in practice extremely difficult to maintain during the successive changes in temperature in the system and seems to be very critical. The technic recommended for the removal of the carbon dioxide from the contents of the receiving flask after the first titration is so very sensitive that the introduction of an error of considerable and indeterminable magnitude by the loss of acetic acid during the boiling out is greatly facilitated.

More recently the method of Kuhn and Roth (6) has been described. These authors have devised an apparatus in which degradation of the sample may be accomplished by alkaline hydrolysis in either aqueous or alcoholic solution, by acid hydrolysis, or by chromic acid oxidation. In order to use the last-named reagent it is necessary to know the structure of the compound being analyzed to account for all the groupings which might yield volatile acids. Alkaline hydrolysis more easily ruptures certain linkages but, in the absence of definite criteria for this, the use of alternative reagents seems to complicate the problem of analysis unnecessarily. Further, the well-known solvent action of alkali on glass makes for undesirable effects on the apparatus. Alcoholic solutions of the reagents are desirable under certain conditions, to provide a more homogeneous reaction mixture. However, the technic is complicated by the necessity for removal of the alcohol prior to the distillation of the volatile acid. Distillation in this method is conducted at atmospheric pressure, successive portions of distillate being titrated separately with 0.01 *N* sodium hydroxide against phenol-

phthalein after a short boiling to remove the carbonic acid and the sulfur dioxide formed when sulfuric acid or *p*-toluene sulfonic acid is used as the hydrolyzing agent. In addition to the objections raised before regarding the boiling of the distillate, this plan of titration of portions is subject to the criticism that it is a fertile source of error, the normal titrimetric errors, individually small, being multiplied by the number of titrations (at least four) to yield a not inconsiderable sum.

Mention may here be made of the method of Bailey and Robinson (1), who saponify by refluxing the sample for several hours in 0.04 *N* sodium hydroxide and titrate the excess alkali with 0.01 *N* hydrochloric acid. While this method is applicable only to substances which do not possess acidic functions either *per se* or as a result of alkaline splitting—e. g., lactones, lactams, and hyperacetylated sugars (see Pirie, 9)—their finding that the error introduced by the absorption of carbon dioxide is negligible is significant. The conditions they employ are such as to make this a prime consideration, due to the great avidity of alkaline solutions for carbon dioxide. It would seem then, that, if this error is negligible under their conditions, it may certainly be dis-

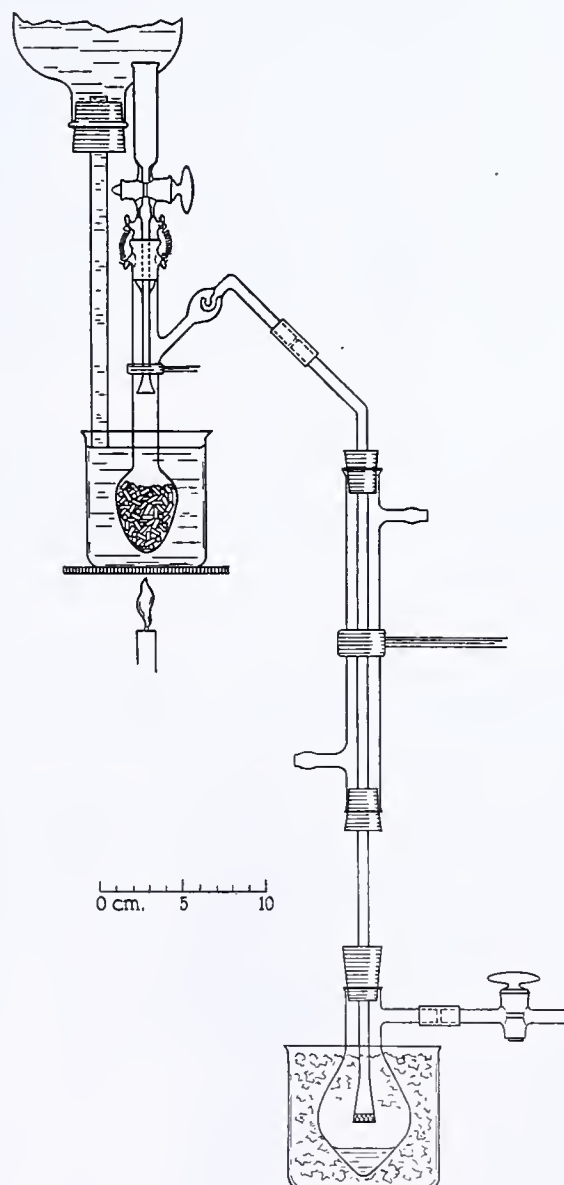


FIGURE 1. DIAGRAM OF APPARATUS

regarded where the solution to be titrated possesses less chemical affinity for carbon dioxide because of its acidity.

In the method described below the hydrolysis is performed with aqueous *p*-toluene sulfonic acid in a simplified apparatus and, following distillation *in vacuo*, the sulfur dioxide and acetic acid are measured by iodometric titrations.

While the time required for an analysis is not reduced, fulfillment of the conditions set forth guarantees accurate results in all cases except where more than one volatile acid is produced by hydrolysis. Excessively high results arise from this last condition. Duplicate analyses show that the precision of the method is high.

Experimental

The apparatus, as shown in Figure 1, is constructed wholly of Pyrex glass, with the joints especially ground to be vacuum-tight with only water as lubricant. The connection between the side arm of the flask and the condenser is glass to glass, sheathed in steamed rubber tubing in order to provide sufficient flexibility to permit tapping the flask. It is important, therefore, that these parts be made of the same diameter tubing.

For the hydrolysis a 25 per cent aqueous solution of *p*-toluene sulfonic acid is employed. In addition the following reagents are required:

1. An approximately 0.01 *N* iodine solution, prepared by dissolving 1.27 grams of analytical reagent iodine in a solution of an equal weight of analytical reagent potassium iodide in freshly boiled distilled water and diluting to 1 liter (or by dilution of an 0.1 *N* solution). This solution need not be standard.
2. An approximately 0.01 *N* sodium thiosulfate solution best prepared by dilution of an aged 0.1 *N* solution, preserved by the addition of 1 per cent amyl alcohol (?). This solution must be standardized at least at intervals of 2 to 3 days. Standardization may most conveniently be effected by means of potassium biiodate.
3. A 0.01 *N* solution of potassium biiodate prepared by weighing out on an analytical balance exactly 325 mg. of the recrystallized and well-desiccated salt and diluting to exactly 1 liter with boiled out distilled water.
4. A 1 per cent solution of soluble starch in saturated sodium chloride solution.
5. A 4 per cent solution of analytical reagent potassium iodate in freshly boiled distilled water.

The whole apparatus, with the exception of the rubber connection which is well steamed, is thoroughly cleaned with chromic acid cleaning mixture, well rinsed, and dried before using. Between successive determinations thorough rinsing with distilled water is sufficient and only the flask need be dried.

A well-ground and thoroughly dried sample of from 4 to 10 mg., accurately weighed by difference on a microbalance, is placed on the bottom of the hydrolyzing flask, preferably using a long-handled charging tube. The flask is then filled about three-quarters full with short pieces (4 to 5 mm. each) of 4-mm. Pyrex rod. (In preliminary trials soft glass beads were used. These quickly became porous as evidenced by their opacity and were discarded in favor of the Pyrex rod which has since been used without deterioration. This has been remarked before in connection with the original Pregl halogen method, where beads were at first used in the combustion tube and were later replaced by a spiral.) The funnel, wet on the ground joint with distilled water, is inserted and fastened with short wire springs. Two milliliters of the sulfonic acid reagent are then added through the funnel and the closed stopcock is sealed with 2 to 3 drops of distilled water added through the funnel. In the analysis of halogen-containing compounds, a few milligrams of silver sulfate should be added.

The side arm of the flask is connected to the condenser by means of the freshly rinsed short section of rubber tubing, a glass-to-glass joint being easily effected. The receiving flask, previously charged with 5 ml. of the 0.01 *N* iodine solution with 1 to 1.5 grams of potassium iodide (conveniently measured out

as a powder by means of a small marked test tube) dissolved therein, is attached to the rubber stopper on the lower end of the condenser and adjusted so that the sintered plate is about 1 cm. above the surface of the liquid. (The majority of the determinations reported here were carried out using a quartz flask as receiver. Substitution of a Pyrex receiver was accompanied by no change in the results.) The side arm of the receiver is capped with a well-washed rubber nipple. The receiver, up to the side arm, is cooled by immersion in a beaker of finely cracked ice, renewed from time to time during the hydrolysis after removal of the water formed by the melting. A stream of cold water is circulated through the jacket of the condenser. The flask is tapped sufficiently to mix the sample intimately with the acid.

An asbestos board is placed as a shield between the burner and the condenser. The mixture is heated by bringing the water in the surrounding beaker to boiling. The level of water in the beaker is maintained during the period of heating by using an inverted bottle containing water, held well above the apparatus, and having a 1-cm. tube reaching just to the desired level in the beaker.

During the course of the heating the flask is vigorously tapped at intervals in order to agitate its contents. Hydrolysis is continued for 1 hour for *O*-acetyl and 2.5 to 3 hours for *N*-acetyl compounds. Where the nature of the linkage is unknown the longer period is, of course, to be employed. At the end of the hydrolysis the hot water is siphoned out of the beaker and replaced by ice-cold water. After leaving the apparatus to cool for about 5 minutes, an aspirator is connected through a manometer and stopcock to the side arm of the receiver and the system is evacuated to a pressure of 50 to 60 mm. The receiver is lifted, together with its cooling beaker, until the sintered plate is about 2 mm. from the bottom of the receiver and the water surrounding the hydrolyzing flask is heated. At first a few very small bubbles are seen to pass through the iodine solution, but the bubbling stops in a few seconds as the pressure is equalized throughout the system. When the fluid in the flask has completely distilled over, aided by occasional tapping, about 1.5 ml. of water are run in through the funnel without either breaking the vacuum or stopping the heating. After the contents of the flask have become dry, a second and finally a third portion of water are introduced in a similar manner. Heating is then continued until the contents of the flask are completely dry and for 5 to 10 minutes thereafter. The receiver is then lowered, using a gentle rotatory motion, until the sintered plate is 2 to 3 cm. above the fluid. The stopcock between the receiver and the gage is closed; the connection between the stopcock and the gage is broken, and then by slowly opening the stopcock the system is brought back to atmospheric pressure, and the burner is extinguished.

The condenser is disconnected from the flask and washed through three times with small volumes of distilled water, flow across the sintered plate being aided by application of suction through the side arm of the receiver. The outside of the lower part of the condenser is washed into the receiver with distilled water; the total volume should be about half its capacity. The solution in the receiver, whose side arm is capped with the rubber nipple, is titrated with the standard thiosulfate, using 2 drops of the starch indicator added toward the end of the titration. To the now colorless solution about 2 ml. of the potassium iodate solution are added, and the receiver is immediately stoppered with a soda-lime tube, placed in a beaker of water at about 35° C., and allowed to stand for 20 minutes. At the end of that time the solution is titrated with the thiosulfate solution, the end point being taken where the blue color which develops during the titration just disappears.

The value from the initial titration is to be subtracted from the value obtained by titration of 5 ml. of the iodine solution in which 1 to 1.5 grams of the potassium iodide are dissolved and 2 to 3 drops of dilute acetic acid added. (It is especially important when measuring the iodine solution from a microburet to wait 1 to 2 minutes before reading the buret; the drainage error may otherwise be considerable.) This latter titration should not be made until the mixture has stood for about 5 minutes at room temperature. The difference so calculated is a correction for the sulfur dioxide and varies from 0.00 to 0.05 ml. Where it exceeds the upper limit the analysis should be rejected. The difference, doubled to account for the dibasicity of the sulfuric acid formed, is deducted from the final titration as a correction for the acid introduced as sulfur dioxide.

TABLE I. REPRESENTATIVE ANALYTICAL RESULTS

No.	Compound	Formula	Moles of Acetyl, Nature of Linkage	Weight of Sample Mg.	Vol. 0.01 N Na ₂ S ₂ O ₃ Corr. Ml.	Acetyl Found %	Acetyl Calcd. %
1	Tetraacetyl nitrophenol- β -galactoside	C ₂₀ H ₂₂ O ₁₂ N	4-O	9.800	8.37	36.74	
2	Triacetyl monoacetone glucose	C ₁₅ H ₂₂ O ₉	3-O	8.400	7.22	36.65	36.70
3	Triacetyl xylosazone	C ₂₃ H ₂₆ O ₆ N ₄	3-O	6.905	5.99	37.30	
4	Theophylline triacetyl rhamnose	C ₁₉ H ₂₄ O ₉ N ₄	3-O	11.380	9.85	37.20	37.26
5	Hexose benzylidene diacetate glucoside	C ₁₈ H ₂₂ O ₈	2-O	7.520	4.94	28.26	
6	Benzylidene anisaldehyde acetate aminoglucoside	C ₂₄ H ₂₇ O ₇ N	1-O	8.102	5.30	28.15	28.39
7	Galactose pentaacetate	C ₁₆ H ₂₂ O ₁₁	5-O	8.320	5.51	28.49	
8	Tetraacetyl galactose phenylosazone	C ₂₆ H ₃₁ O ₈ N ₄	4-O	9.095	6.20	28.43	28.50
9	Mannitol hexaacetate	C ₁₈ H ₂₆ O ₁₂	6-O	8.500	4.61	23.33	23.50
10	Aldehydoglucose oxime hexaacetate	C ₁₈ H ₂₆ O ₁₂ N	6-O	8.479	1.92	9.50	9.70
11	p-Nitrobenzyl glycoside of triacetyl galacturonic acid methyl ester	C ₂₀ H ₂₂ O ₁₂ N	3-O	5.824	7.76	55.06	55.10
12	Heptaacetyl methyl ester of gentiobiuronic acid	C ₂₇ H ₃₆ O ₁₉	7-O	7.021	5.32	32.60	32.62
13	Aceturic acid	C ₄ H ₇ O ₂ N	1-N	4.986	6.86	59.17	59.41
14	Acetanilide	C ₈ H ₉ ON	1-N	7.317	9.80	57.59	57.69
15	p,p'-Diacetyl phenylenediamine	C ₁₀ H ₁₂ O ₂ N ₂	2-N	5.694	4.79	36.18	36.27
16	Nitro-p,p'-diacetyl phenylenediamine	C ₁₀ H ₁₁ O ₄ N ₃	2-N	6.178	8.28	57.61	57.69
17	β -Glucose oxime hexaacetate	C ₁₈ H ₂₆ O ₁₂ N	5-O; 1-N	6.110	6.83	48.04	48.08
18	β -Glucose semicarbazone pentaacetate	C ₁₇ H ₂₅ O ₁₁ N ₃	4-O; 1-N				

The acetyl content is given by the formula

$$\% \text{CH}_3\text{CO} = 100 \times \frac{\text{volume of thiosulfate (corr.)} \times \text{factor of solution} \times 0.4302}{\text{weight of sample}}$$

Representative analytical results are presented in Table I.

Discussion

The method described here is calculated to bring microacetyl determinations, which have hitherto been regarded as not entirely satisfactory for general use, into line with the more common organic microanalytical procedures as regards accuracy and precision. The distillation is improved over previous methods by omitting an air stream and establishing uniform low pressure throughout the apparatus. Introduction of a sintered glass plate at the lower end of the condenser ensures complete absorption of the distillate in the receiving fluid, while the conditions prevailing throughout the manipulation have rendered completely negligible any error which might be due to carbon dioxide. In fact, a blank analysis made with glucose required no 0.01 N thiosulfate, showing complete absence of carbon dioxide. However, these experiments were performed in a well-ventilated microanalytical laboratory, and it is readily conceivable that other results might be obtained elsewhere.

While it may appear that, in comparison with other methods, the times recommended for the hydrolysis are unnecessarily long, the employment of these conditions ensures complete hydrolysis regardless of the nature of the linkages. Since the operation proceeds with very little attention during the hydrolysis, the increase in time is unimportant, especially when the general use of the longer period may so often save the repetition of an analysis. It is true that in some cases hydrolysis is complete in 20 to 30 minutes but there is no way in which such may be identified beforehand. In fact, the β -glucose oxime hexaacetate (compound 17 in Table I), where one acetyl is linked to nitrogen and the other four to oxygens, gave satisfactory figures with only 30 minutes' hydrolysis.

In several cases the 1.5 hours' hydrolysis recommended by Friedrich (5) for N-acetyl was found to be insufficient, values in concordance with theory being obtained only after 2.5 to 3 hours. Using aceturic acid (acetylglucine, compound 13 in Table I) accurate figures were obtained in 2.5 hours, while poorer results were reported by Kuhn and Roth (6) who used alkali for the same time. Freudenberg and Soff

(3) had to hydrolyze their sample 11 to 15 times to get satisfactory results.

It has always been felt that quantitative distillations at reduced pressure were not suitable for microanalytical procedures, especially where the substance sought has a fairly high vapor pressure at ordinary temperatures. The method of Kuhn and Roth (6) was designed in part to overcome the weakness of such a procedure. However, quantitative distillation of acetic acid at atmospheric pressure is also accompanied by some uncertainty. Absence of a difficultly regulated gas stream and improved absorption of the distillate in the receiver of the sintered plate have made quantitative recovery of the distillate a routine requiring no elaborate precautions. With the apparatus and method reported here there is no necessity for the frequent changes of temperature prescribed by Friedrich (5) and the extra distillation recommended here constitutes an additional guarantee of complete removal of the volatile acid.

Summary

An apparatus is described and a procedure recommended for the quantitative determination of acetyl in 4–10 mg. of substance. A method for the quantitative distillation of volatile substances *in vacuo* for analytical purposes is elaborated.

Acknowledgment

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Determination of Volatile Fatty Acids by the Partition Method

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THE volatile fatty acids most frequently encountered in fermentation studies are formic, acetic, propionic, and butyric. Usually but one or two of these acids are present, although three- and four-acid mixtures occur. Experience has shown that there are three conditions under which the determination of these four acids will usually be carried out: (1) In routine studies and in plant control work the number and identity of the acids present are always known and the analysis consists merely in determining the percentage of each acid present. (2) During physiological investigations in which the fermentations take place under varying environmental conditions, or when mixed cultures or new species are being used, doubt often exists as to the exact qualitative composition of the fatty acid mixture. In such mixtures, the identification of the acids present by the preparation of organic derivatives or by fractional crystallization of the silver salts requires too much time, except for the final identification of the acids produced by a new species. (3) Higher fatty acids may be produced in small amounts in addition to the four acids mentioned above, and cause serious errors in the analysis of the other acids. Also, lactic, pyruvic, and possibly other hydroxy or keto acids may be present, and these are sufficiently volatile with steam to be partly carried into the distillate with the volatile acids. All such acids will be referred to here as "foreign" acids. They may have been produced by the fermentation, or added intentionally to the medium as part of the substrate.

The purpose of this paper is to show the application of the partition method (4, 7) to the rapid analysis of volatile fatty acid mixtures under the above conditions. The partition method has been used in this laboratory for the past 5 years and has been modified from time to time to meet the demands of fermentation research.

Preparation of Fermentation Liquors for Analysis

It is often desirable to separate certain neutral volatile products (alcohols, acetone, etc.) from fermentation liquors before the volatile acids are removed. If unfermented sugar is present, it is not advisable to neutralize the liquor before distilling off the alcohols. The pH of the solution is adjusted to about 4 with sulfuric acid (just blue to congo red paper) and the neutral products, together with part of the volatile acids, are distilled. The distillate is neutralized with sodium hydroxide and distilled until all of the neutral products are removed—i. e., one-half the volume is distilled. The two residues are combined, the pH is again adjusted to 4, and the liquid distilled with steam until 2 liters of distillate are collected. The volume of liquid in the distilling flask should be kept between 75 and 150 cc.

If the concentration of the acids in the 2 liters of distillate is too low for the analysis, the entire distillate should be neutralized with alkali and evaporated to 150 cc. The residue is acidified, saturated with magnesium sulfate, and distilled with steam as described by Olmstead, Whitaker, and Duden (3). One liter of distillate should be collected. Alternatively, if greater concentration is desired, the original distillate may be neutralized with standard barium hydroxide and evaporated to the desired volume. Sulfuric acid exactly equivalent

to the barium hydroxide is added and the barium sulfate removed by decantation and filtration. In this alternative procedure certain contaminating hydroxy acids will be present in the solution, and may interfere with subsequent analysis. In the procedures given below the concentration of acids should be about 0.03 *M* with respect to total volatile acid present.

Conventions Used

To facilitate description of the method and to make possible the use of the nomograms (Figures 1 and 2), certain abbreviations and conventions have been adopted. The percentage of each acid present will be expressed as molar percentage—the per cent of the total molarity which is due to each acid present.

Assuming that the entire acid distillate contains the equivalent of 10 cc. of 1.0 *M* acetic acid, 10 cc. of 1.0 *M* propionic acid, and 30 cc. of 1.0 *M* butyric acid, or 50 cc. of 1 *M* acid in all, then the molar percentage of acetic acid is $10/50 \times 100$ or 20, that of propionic is 20, and that of butyric is 60. If the molar percentages of formic, acetic, propionic, and butyric acids are represented by *F*, *A*, *P*, and *B*, respectively, the composition of the mixture may be written $A + P + B = 100$, in which $A = 20$, $P = 20$, and $B = 60$. Since only monobasic acids are considered, the terms "molarity" and "normality" have identical significance.

Principles of the Partition Method

The partition method is based on the distribution of the fatty acids between two immiscible solvents, such as water and ethyl ether, when dilute water solutions of the acids are shaken with acid-free ether in separatory funnels. In this paper the percentages of the acids which remain in the aqueous phase are taken as the partition constants. The four sets of partition constants shown in Table I were determined as follows:

Solutions of the pure acids in water were adjusted to approximately 0.03 *M* each. For each of the constants in column 1 of Table I, 60 cc. of the acid solution and 100 cc. of pure, acid-free ethyl ether were shaken vigorously in a separatory funnel for 1 minute. Two minutes were allowed for the two phases to separate, and 50 cc. of the aqueous phase were removed and titrated with 0.05 *N* alkali in presence of phenolphthalein, the cubic centimeters of alkali required being designated as *N*₁. The cubic centimeters of alkali required to titrate 50 cc. of the original acid solution were designated as *N*₂. The partition constant for the acid is $N_1/N_2 \times 100$. The other constants in columns 2 to 4 (Table I) were determined in like manner, using the volumes of acid solution and of ether shown in the column headings.

TABLE I. PARTITION CONSTANTS OF ORGANIC ACIDS

	60 cc. of Acid 100 cc. of Ether	100 cc. of Acid 20 cc. of Ether	150 cc. of Acid 20 cc. of Ether	60 cc. of Acid 200 cc. of Ether
Formic	63.5	90.8	92.4	48.1
Acetic	58.2	88.8	91.8	42.2
Propionic	27.2	78.0	85.9	16.2
Butyric	10.3	57.3	73.5	5.0
Valeric	7.5	39.0	55.2	4.3
Lactic	84.5	92.7	93.0	77.5

To secure thorough mixing of the two phases it is important that the total capacity of the separatory funnels be 50 to 100 cc. greater than the combined volumes of ether and acid solutions used.

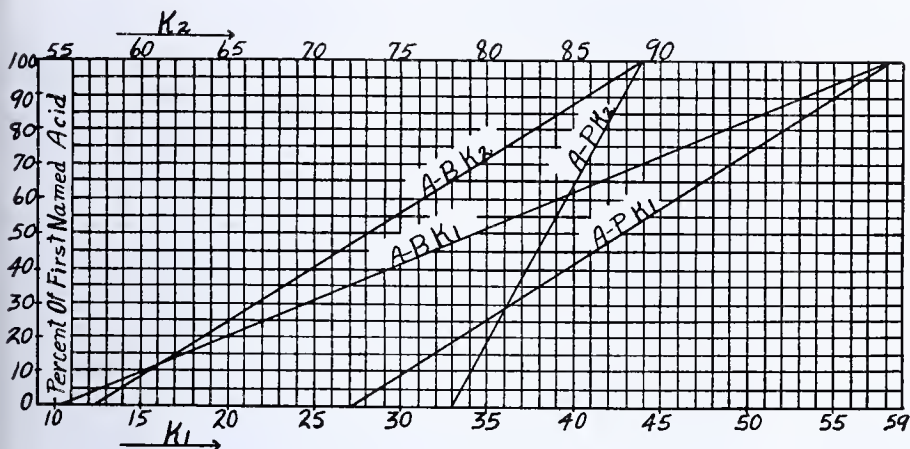


FIGURE 1. NOMOGRAM FOR DETERMINATION OF ACIDS IN TWO-ACID MIXTURES

In the following discussion the partition constants of the individual acids will be referred to as f_1 , a_1 , p_1 , and b_1 , for the constants in column 1 of Table I. The subscripts denote the set of constants referred to in Table I. These constants vary somewhat with concentration of the acids in solution. The constants in Table I were determined for the acids in 0.03 M solutions and are valid only for concentrations ranging from 0.02 to 0.04 M.

If two or more acids are together in a solution, each has its own partition constant and acts independently of the other acids present. If a mixture contains acetic and propionic acids in equimolar portions—i.e., if $A = 50$ and $P = 50$ —the partition constant obtained by shaking 60 cc. of the acid solution with 100 cc. of ether (column 1, Table I) is

$$50 \times 0.582 + 50 \times 0.272 = 42.7 = K_1$$

The partition constants are written decimally in all calculations as a matter of convenience. K_1 designates the partition constant for any mixture of acids when 60 cc. of acid solution and 100 cc. of ether are used to determine the constant. Likewise K_2 is found by using 100 cc. of acid solution and 20 cc. of ether as shown in column 2 of Table I, etc.

Since no other mixture of acetic and propionic acids could give 42.7 as the value for K_1 , it follows conversely that if one partition constant, such as K_1 , is determined for the mixture, the percentage of each acid present can be found. This may be done either graphically or by means of equations. If two acids are present in solution only one partition constant need be determined, but there must be two equations. Using a mixture of acetic and propionic acids as an example and the conventions already described, equations may be written as follows:

$$\begin{aligned} a_1A + p_1P &= K_1 \\ A + P &= 100 \end{aligned}$$

These equations may be solved for A and P in terms of K_1 . Similar equations may be written for any two-acid mixture, and such equations are given below. The graphical method is more convenient. If K_1 is determined for a mixture of acetic and propionic acids it is only necessary to locate K_1 on the $A-PK_1$ diagonal of Figure 1 and read the molar percentages of A and P on the ordinate. Diagonal lines are given for acetic-propionic and acetic-butyric acid mixtures for both K_1 and K_2 values. Similar charts may be made for any two-acid mixtures. The construction of Figure 1 is given below.

If three acids, such as acetic, propionic, and butyric, are present it is necessary to determine two partition constants, K_1 and K_2 , and Figure 2 is used as described below.

Procedure

DETERMINATION OF ACIDS IN TWO-ACID MIXTURES. The concentration of acid in the solution should be about 0.03 M.

Bring the acid solution and the ether to be used to a temperature of 25° C. Pipet 60 cc. of the acid solution into a separatory funnel of about 250-cc. capacity, add 100 cc. of pure ethyl ether, and shake the mixture vigorously for 1 minute. Towels should be wrapped around the funnels to prevent heating by the hand. If the temperature of the laboratory differs more than $\pm 3^\circ$ C. from 25° C., precautions should be taken to keep the temperature of the mixture at approximately 25° C. After the mixture is shaken, allow it to stand for 2 minutes for the two phases to separate. Remove 50 cc. of the aqueous phase and titrate with 0.05 N sodium hydroxide (phenolphthalein), designating the cc. of alkali as N_1 . Titrate 50 cc. of the original mixture, the cc. of alkali required being N_2 . Calculate K_1 —i.e., $N_1/N_2 \times 100$.

This procedure applies only when the two acids present are known. If they are acetic and butyric acids, locate K_1 on the $A-BK_1$ line in Figure 1. If acetic and propionic acids are present, locate K_1 on the $A-PK_1$ line. Read the percentage of acetic acid on the left-hand ordinate. Subtract from 100 to get the molar percentage of the other acid. From these data calculate the amount of each acid present in the original solution. For example, if the 50 cc. of acid solution titrated contained 30 cc. of 0.05 N acid and if there were 2 liters of the solution, there would be 60 cc. of 1 N acid present. If analysis showed 70 molar per cent of acetic acid and 30 per cent of butyric acid, there would be 42 cc. of 1 N acetic and 18 cc. of 1 N butyric acids present.

ANALYSIS OF THREE-ACID MIXTURES, ONE OF WHICH IS FORMIC ACID. The partition constants of formic and acetic acids are so close together (Figure 3) that accurate determinations of either in the presence of the other cannot be made by the partition method. The formic acid in such mixtures may be determined by the method of Auerbach and Zeglin (1), of Osburn, Wood, and Werkman (4), or of Weihe (6). Express the amount of formic acid found as molar per cent of the total acid as follows:

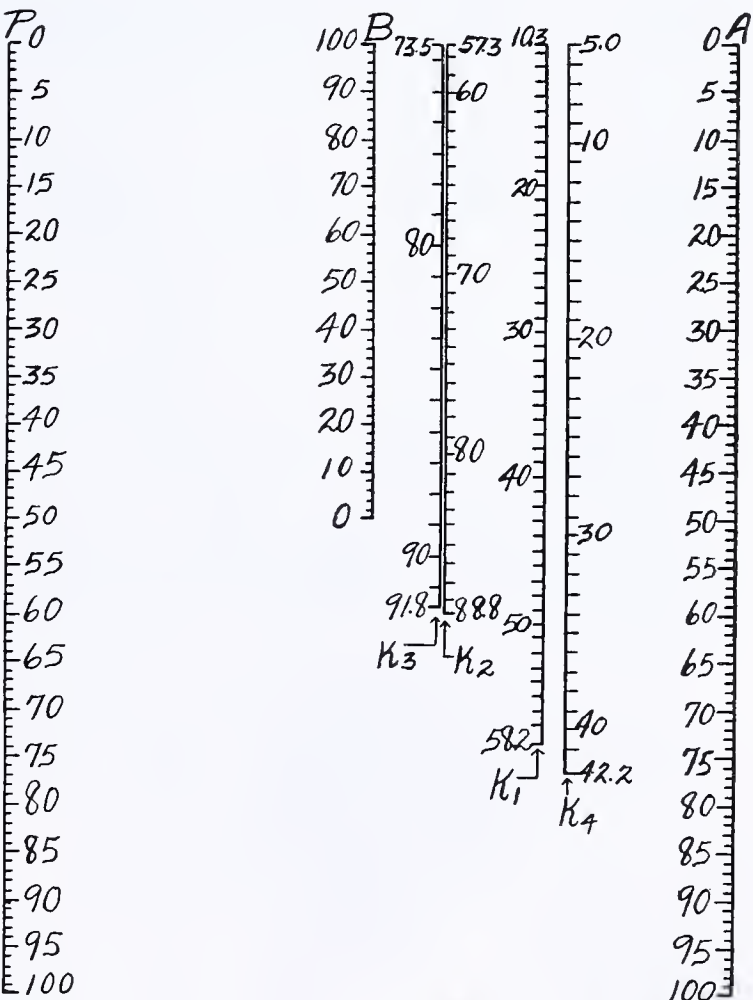


FIGURE 2. NOMOGRAM FOR DETERMINATION OF ACIDS IN THREE-ACID MIXTURES

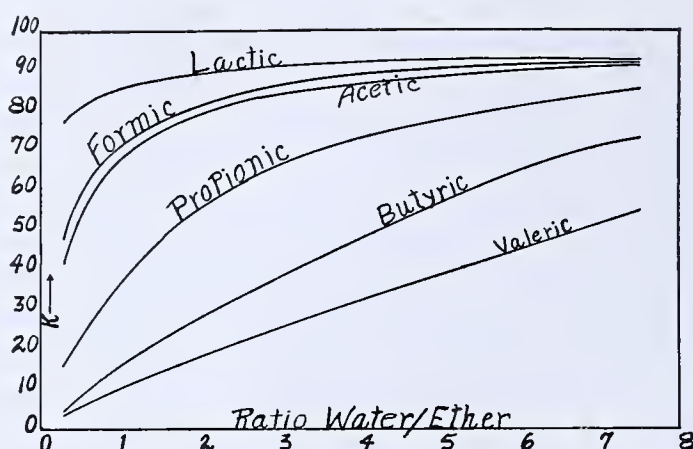


FIGURE 3. PARTITION CONSTANTS FOR VARYING RATIOS OF WATER TO ETHER USED IN THEIR DETERMINATION

Suppose the total acid solution contains 50 cc. of 1 *M* acid and that 0.230 gram of formic acid is found present. The cc. of 1.0 *M* formic acid will be $\frac{0.230}{0.046} = 5.0$ cc. (1 cc. of 1 *M* formic acid contains 0.046 gram).

According to the conventions $F = \frac{5}{50} \times 100 = 10$ molar per cent. To determine the other acids find K_1 for the mixture as described above. Before using the nomogram (Figure 1) K_1 has to be corrected for the known percentage of formic acid and a new constant K_1^1 calculated as follows:

$$K_1^1 = \frac{K_1 - f_1 F}{\frac{100 - F}{100}}$$

Locate K_1^1 then on the diagonal corresponding to the two acids known to be present (aside from formic) and find the percentages of the two acids from the ordinate. Multiply each of these percentages by $\frac{100 - F}{100}$ to get the true percentages of the two acids in the solution. Example: The constant, K_1 , for mixture 5, Table II, was 40.25 and F was equal to 10.0. Hence

$$K_1^1 = \frac{40.25 - 0.635 \times 10}{\frac{100 - 10}{100}} = 37.66$$

This value of K_1^1 was located on the $A-PK_1$ line and gave 33.0 and 67.0 for A and P . These two values, each multiplied by $\frac{100 - 10}{100}$ (i. e., $\frac{100 - F}{100}$) gave 29.8 and 60.2 for A and P , respectively. Thus $F + A + P = 100$. The constants given in Table II are the K_1 values. The results shown in Table II are representative.

METHODS OF CONFIRMING QUALITATIVE ASSUMPTIONS. The exact qualitative composition of an acid mixture is sometimes in doubt. A mixture may be known to contain acetic and butyric acids and the presence of another acid may be suspected, or it may not be known whether a mixture is one of acetic and butyric acids or acetic and propionic acids, etc. The procedures given above tell nothing as to the accuracy of the analysis. Confirmation is offered by the following simple procedure:

TABLE II. DETERMINATION OF ACIDS BY PARTITION METHOD

Expt.	Acid Present				Acid Found				K_1	K_2
	Formic %	Acetic %	Propionic %	Butyric %	Formic ^a %	Acetic %	Propionic %	Butyric %		
1	0	33.3	66.6	0	..	33.0	67.0	..	37.4	82.4
2	0	25.0	75.0	0	..	25.2	74.8	..	35.05	80.5
3	0	83.4	0	16.6	..	83.7	..	16.3	50.4	83.4
4	0	30	0	70.0	..	30.2	..	69.8	24.63	66.8
5	10	30	60	0	10	29.8	60.2	..	40.25	83.0
6	10	70	0	20	10	70.1	..	19.9	49.2	82.2
7	0	33.3	33.3	33.3	..	32.8	35.0	32.0	32.0	75.0
8	0	50	20	30	..	49.8	20.2	30.0	37.7	77.3
9	10	50	30	10	10	49.4	31.8	9.0	44.9	82.9
10	20	20	20	40	20	20.0	22.0	38.0	34.2	74.8

^a Actual amounts present. No determinations were made on formic acid.

Find K_1 for the mixture. Determine K_2 for the mixture by shaking 100 cc. of the acid solution with 20 cc. of ether and titrating 50 cc. of the aqueous phase and 50 cc. of the original solution. Calculate K_2 in the same manner as K_1 . Assume (as an example) that the mixture is thought to contain acetic and propionic acids and no others. Locate K_1 on the $A-PK_1$ diagonal, move horizontally to the same ordinate on the $A-PK_2$ diagonal, and read, at the top of the chart, a corresponding value of K_2 . Call this value K_{2c} . If only acetic and propionic acids are present, K_2 , the experimental value, and K_{2c} should agree in value to within 0.3 or 0.4 unit. Usually these two values agree within 0.2 unit.

If appreciable quantities of other acids are present or if the qualitative assumptions were wrong, there would be a large difference between K_2 and K_{2c} . Suppose, for example, that mixture 3, Table II, had been assumed to contain acetic and propionic acids and that the above procedure had been carried out. The K_2 value found for this mixture was 83.4 and K_{2c} (assuming an acetic-propionic mixture) was 86.0—i. e., $K_2 - K_{2c} = -2.6$. If mixture 2, Table II, had been thought to contain acetic and butyric acids $K_2 - K_{2c}$ would have been $80.5 - 73.4 = +7.1$. Making correct assumptions, $K_2 - K_{2c}$ for mixture 3 is -0.2 and for mixture 2, $K_2 - K_{2c} = -0.1$.

Such false assumptions are not likely to be made but serious errors sometimes occur in the determination of acetic, propionic, and butyric acids because of the presence of small amounts of lactic or pyruvic acid or of acids above butyric acid in the series. The differences ($K_2 - K_{2c}$) caused by a few such "foreign" acids in two-acid mixtures are shown in the first seven mixtures of Table III. It has been found that the algebraic sign of $K_2 - K_{2c}$ will always be negative if the numerical values of the partition constants of the foreign acid are either greater or smaller than the constants of the two acids being determined. Referring to the curves of Figure 3, if any acid shown is taken as a "foreign" acid in the analysis of an acetic-propionic acid mixture, for example—the $K_2 - K_{2c}$ difference will be negative, and the curve of this foreign acid will be outside the curves of the acids being determined. For an acetic-butyric acid mixture, propionic acid would give a positive value for $K_2 - K_{2c}$, since the curve lies between the curves for these two acids. Otherwise, for an acetic-valeric acid mixture, both propionic and butyric acids would give positive values. Beyond this the procedure offers no means of identifying the "foreign" acids present.

If formic acid is present both K_1 and K_2 should be corrected as described above:

$$K_1^1 = \frac{K_1 - f_1 F}{\frac{100 - F}{100}} \text{ and } K_2^1 = \frac{K_2 - f_2 F}{\frac{100 - F}{100}}$$

The K_1^1 and K_2^1 values calculated are then used in the same manner as K_1 and K_2 given above.

DETERMINATION OF ACETIC, PROPIONIC, AND BUTYRIC ACIDS IN A MIXTURE. Determine K_1 and K_2 as described above. Locate K_1 on the K_1 line of Figure 2 and K_2 on the K_2 line. Lay a straight edge across these two points and read A on the A line, P on the P line, and B on the B line of the chart.

If formic acid is present, determine F and calculate K_1^1 and K_2^1 exactly as described above. Locate K_1^1 on the K_1 line and K_2^1 on the K_2 line and read values of A , P , and B . Multiply each of the values by $\frac{100 - F}{100}$ to get the percentage of each acid present. The results shown in the last four mixtures of Table II are typical of many analyses made in this manner. Equations for A , P , and B in terms of K_1 and K_2 are given below.

It is possible to detect the presence of "foreign" acids in mixtures of formic, acetic, propionic, and butyric acids. The constants in columns 3 and 4 of Table I and the lines K_3 and K_4 on Figure 2 are for this purpose. If acids above butyric acid in the series are thought to be pres-

TABLE III. DETECTION OF FOREIGN ACIDS IN MIXTURES OF VOLATILE FATTY ACIDS

Composition of Mixture			Foreign Acid, %							
F	A	P		K ₁	K ₂	K ₃	K ₄	K ₂ - K _{2c}	K ₃ - K _{3c}	K ₄ - K _{4c}
..	40	50	..	Formic, 10	43.2	83.6	-0.02	..
..	40	..	50	Formic, 10	34.8	73.3	-0.15	..
..	80	10	..	Butyric, 10	50.3	84.6	-1.5	..
..	30	60	..	Valeric, 10	33.7	77.5	-2.7	..
10	40	..	40	Valeric, 10	34.4	71.2	-1.9	..
..	70	..	20	Lactic, 10	51.5	83.0	-1.3	..
..	50	..	30	Propionic, 20	37.7	77.3	+2.3	..
10	50	30	10	None	44.9	82.9	88.4	31.5	-0.1	+0.2
..	20	30	40	Lactic, 10	32.3	73.3	82.7	22.9	-0.2	+0.9
..	30	20	30	Lactic, 10
..	30	20	30	plus Valeric, 10	35.2	72.6	81.6	25.6	-0.8	+0.8
..	40.6	20.2	30.2	Valeric, 9.1	33.1	72.8	82.0	22.5	-0.5	-0.05

ent, determine K₁, K₂, and K₃ by using the volumes of acid solution and ether shown in Table I. Locate K₁ and K₂ as described, and read K_{3c} on the K₃ line at the point of intersection of K₃ and the straight edge. If appreciable quantities of higher acids are present, K₃ - K_{3c} will differ by more than 0.4 unit.

Nonvolatile acids, such as lactic or pyruvic, are detected by using K₄ in the same manner. The data for the last four mixtures of Table III show that K₃ - K_{3c} is not significantly affected by the nonvolatile acids, and that K₄ - K_{4c} does not show the presence of highly volatile acids (valeric, capric, caproic, etc.).

This latter procedure can be used only to detect large errors in analysis. As the mixtures become more complex, the differences in the K and K_c values become less, and it is more difficult to get satisfactory agreement between K₃ and K_{3c} or K₄ and K_{4c} with mixtures of known purity. If the procedure is used with suitable precaution it can be of considerable service.

Construction of Nomograms

Figure 1 is drawn on ordinary cross-section paper. It is possible to secure paper such that the K₁ and K₂ scales may be read directly to 0.1 or 0.2 unit. The K₁ values are on the horizontal axis and the diagonals A-PK₁ and A-BK₁ are drawn as shown. The K₂ values are placed at the top merely as a matter of convenience. The K₂ values—i. e., a₂, f₂, and b₂ of Table I—are used when drawing the A-BK₂ and A-PK₂ lines. The two systems are entirely independent of each other and the K₂ scale need not have the same number of lines of the cross-section paper per unit as the K₁ scale.

Figure 2 may be drawn to any convenient size. The A and P lines may be made 250 mm. in length and 200 mm. apart. The B line is exactly half-way between A and P and has half their length. The lines for the four constants K₁. . . K₄ terminate on the diagonal from P = 0 to A = 100. Their upper ends are on the line from A = 0 to P = 0 which passes through the point B = 100. To calibrate the K₁. . . K₄ lines, use the corresponding constants for the pure acids given in Table I. Each line is calibrated downward from the value of the constant for butyric acid to that for acetic acid. Each of the lines, K₁. . . K₄, is located laterally by the expression

(a - b) / (p - b) / (1 + a - b / p - b) D

where D is the distance between the A and P lines and a, p, and b are the constants of Table I corresponding to the line being located. The intervals so calculated are measured from the P line.

Discussion

The acids used for the determination of the partition constants were purified by several redistillations, taking for each redistillation the fraction nearest the correct boiling point of the pure acid. It has always been possible for different in-

dividuals to duplicate partition constants when working with the same purified sample; but when different acids have been purified and used some discrepancies have been found. Obviously the difficulty lies in the purification of the acids. The many different values published for the Duclaux constants of these same acids have probably arisen in part from the same cause. The constants given in Table I were taken as average values of carefully purified acids, and the calculations given below are based upon them. It is possible that others may be able to use the methods given here without having to deter-

mine new sets of constants and standardize the apparatus, as has always been necessary with the Duclaux (2) method.

The following equations give the percentages of the acids in terms of the constants used. Terms for formic acid (as known values) are included in each equation. If formic acid is not in the mixture, the formic acid term becomes zero and has no effect on the other values. For acetic-propionic acid mixtures, using K₁

a₁A + p₁P = K₁ - f₁ F
A + P = 100 - F

from which, substituting the constants in Table I

A = (K₁ - 100 p₁) / (a₁ - p₁) - (f₁ - p₁) / (a₁ - p₁) F = 3.226 K₁ - 87.75 - 1.17 F (1)

P = (K₁ - 100 a₁) / (p₁ - a₁) + (a₁ - f₁) / (p₁ - a₁) F = 187.73 - 3.226 K₁ + 0.17 F (2)

For acetic-butyric acid mixtures

a₁ A + b₁ B = K₁ - f₁ F
A + B = 100 - F

from which A = (K₁ - 100 b₁) / (a₁ - b₁) - (f₁ - b₁) / (a₁ - b₁) F = 2.088 K₁ - 21.5 - 1.11 F (3)

B = (K₁ - 100 a₁) / (b₁ - a₁) + (a₁ - f₁) / (b₁ - a₁) F = 121.5 - 2.088 K₁ + 0.11 F (4)

For acetic-propionic-butyric acid mixtures which may also contain formic acid and for which K₁ and K₂ are determined, the following equations may be solved for A, P, and B:

0.582 A + 0.272 P + 0.103 B = K₁ - 0.635 F
0.888 A + 0.78 P + 0.573 B = K₂ - 0.908 F
A + P + B = 100 - F

from which

A = 164.71 + 4.508 K₁ - 3.68 K₂ - 1.161 F (5)

P = 10.432 K₂ - 6.86 K₁ - 529.1 + 0.155 F (6)

B = 462.62 + 2.35 K₁ - 6.75 K₂ + 0.0135 F (7)

The procedures given in this paper as confirmatory tests should be used for the most part as time-saving devices. The extra time required to determine K₂ and to apply the procedure does not exceed 10 minutes, and experience has shown that if for two acid mixtures K₂ - K_{2c} is within 0.2 or 0.4 unit, it may safely be assumed that the analysis is correct both quantitatively and qualitatively and no extended search for other acids is necessary. Such assurance is a great satisfaction in fermentation work. Similar methods may be developed for mixtures of acids other than those given here.

The effect of any "foreign" acid on the difference K₂ - K_{2c} can be calculated if the partition constants, x₁ and x₂, and the molar percentage, X, of the acid are known. If acetic and propionic acids are determined in the presence of the foreign acid by using Figure 1, it is obvious that false readings, A_x and P_x, will be obtained. If x₁ and X are substituted in Equations 1 and 2 above they become:

$$A = \frac{K_1 - 100 p_1}{a_1 - p_1} - \frac{(x_1 - p_1)}{(a_1 - p_1)} X \quad (8)$$

$$P = \frac{K_1 - 100 a_1}{p_1 - a_1} + \frac{(a_1 - x_1)}{(p_1 - a_1)} X \quad (9)$$

The last term in each of these equations shows the manner in which A_x and P_x must be corrected in order to obtain A and P , the correct molar percentages of acetic and propionic acids in the mixture. Call these terms the correction factors for X .

The value of K_2 determined experimentally is

$$K_2 = a_2 A + p_2 P + x_2 X$$

The value of $K_2 c$, determined as described above is

$$K_2 c = a_2 A_x + p_2 P_x$$

Hence

$$K_2 - K_2 c = a_2 (A - A_x) + p_2 (P - P_x) + x_2 X \quad (10)$$

In these equations $A - A_x$ and $P - P_x$ represent the numerical values of the correction factors for X . By substituting the correction factors in Equations 8 and 9 for $A - A_x$ and $P - P_x$ in Equation 10 we obtain

$$K_2 - K_2 c = \frac{p_2 (a_1 - x_1)}{(p_1 - a_1)} X - \frac{a_2 (x_1 - p_1)}{(a_1 - p_1)} X + x_2 X \quad (11)$$

The effect of any third acid on the analysis of any two-acid mixtures may be calculated by substituting the constants of the acids concerned in Equation 11. By similar methods the effect of foreign acids on $K_3 - K_3 c$ and $K_4 - K_4 c$ for acetic-propionic-butyric acid mixtures may be calculated. Using the constants in Table I

$$K_3 - K_3 c = (0.02554 x_2 - 0.6204 x_1 - 0.382) X + x_3 X$$

$$K_4 - K_4 c = (0.2 x_1 - 0.909 x_2 - 0.07) X + x_4 X$$

The molar percentage of a "foreign" acid is seldom known in fermentation studies. These calculations are intended to be of use when procedures are being worked out for the analysis of various acid mixtures.

The methods given here reach their maximum effectiveness only when the proper sets of partition constants are selected. In Figure 3 the partition constants have been plotted against the ratios of acid solution to ether used in determining the constants. The ratios range from 0.3 (60 cc. of solution and 200 cc. of ether) to 7.5 (150 cc. of solution and 20 cc. of ether). For the K_1 system (Figure 1) the ratio is 0.6 and for the K_2 system 5.0. These two constants were used for the two-acid mixtures given above because calculations by means of Equation 11 showed that they gave the maximum magnitude to the difference, $K_2 - K_2 c$, when adjacent acids were present as "foreign" acids—i. e., they give the confirmatory procedure its maximum sensitivity.

If 60 cc. of acid and 25 cc. of ether were used to get K_1 , a better differentiation between acetic and butyric acids would be obtained, but no possible value of K_2 could be found to give a suitable difference, $K_2 - K_2 c$.

It can be seen from Figure 2 that for three-acid mixtures the spacing of the K_1 and K_2 lines largely determines the accuracy of the method. If constants are used which place the K_1 and K_2 lines close together the method becomes useless. The expressions used to calculate the spacing of K_1 and K_2 on Figure 2 show that their relative positions are determined by the ratios of $\frac{(a_1 - p_1)}{(p_1 - b_1)}$ and $\frac{(a_2 - p_2)}{(p_2 - b_2)}$. If constants had been selected which made these ratios equal in value, the K_1 and K_2 lines would coincide. If simultaneous equations were used to calculate A , P , and B , the equations under these conditions would be indeterminate and no solution would be

possible. In general, if the constants p_1 and p_2 for propionic acid are spaced at proportionately equal intervals between $a_1 - b_1$ and $a_2 - b_2$, the equations are indeterminate, and K_1 and K_2 will coincide on Figure 2. By using the ratios of 0.6 and 5.0 for K_1 and K_2 , it can be seen from Figure 3 that the constants for propionic acid have been made to approach the constant of acetic acid for K_1 and to approach the constant for butyric acid for K_2 , thereby spacing K_1 and K_2 at the maximum distance apart in Figure 2. In terms of simultaneous equations the determinants are made larger.

Distillation methods, such as the Duclaux method (2) and the Virtanen and Pulkki modification (5) of the Duclaux method, do not offer the advantages given above for the partition method.

In the Virtanen and Pulkki procedure one-fourth and one-half of the volume of solution are distilled and two distillation constants are calculated which correspond to the two partition constants used here. They are, for the one-half volume, $a_1 = 36.6$, $p_1 = 57.7$, $b_1 = 74.0$, and, for the one-fourth volume, $a_2 = 17.2$, $p_2 = 30.8$, and $b_2 = 43.0$. For two-acid mixtures $K_{1/2}$ is used and the results are probably as accurate as they are for the partition method. The other constant, $K_{1/4}$, cannot be used successfully, however, in the detection of foreign acids. If these two sets of constants (a_1, p_1, b_1 , and a_2, p_2, b_2) are used to construct a nomogram such as Figure 1, for a mixture of acetic and propionic acids which contains 10 per cent of butyric acid as a "foreign" acid, the calculated difference $K_{1/4} - K_{1/4} c$, corresponding to the authors' $K_2 - K_2 c$, has a value of only 0.14 as compared to the authors' value of 1.5 (mixture 3, Table III). It has been shown above that if mixture 2 (Table II) had been falsely assumed to be a mixture of acetic and butyric acids, $K_2 - K_2 c$ would have been +7.1. For the same mixture under the same conditions $K_{1/4} - K_{1/4} c$ is only 0.6. For mixture 3 (Table II), assuming an acetic-propionic acid mixture, $K_2 - K_2 c$ would be -2.6 and $K_{1/4} - K_{1/4} c$ would be 0.22. For confirming the analysis the partition method apparently has 10 times the sensitivity of the distillation method.

For three-acid mixtures the two constants are used as they are for the partition method, except that Virtanen and Pulkki did not use the equation $A + P + B = 100$ but used $A + P + B = \text{cc. of } 0.1 N \text{ acid}$. If their two sets of constants are used to construct a nomogram similar in size to Figure 2, the $K_{1/4}$ and $K_{1/2}$ lines would be only 3.3 mm. apart as compared to 26 mm. for K_1 and K_2 . Any error which occurred in the determination of $K_{1/4}$ or $K_{1/2}$ would cause about eight times as much error in A , P , and B as would an error of equal magnitude in K_1 or K_2 . Experience with the distillation methods and with the partition method indicates that about the same errors are to be expected in the determination of the constants in the different procedures.

The ethyl ether used should be free of acid. It is sometimes necessary to purify the ether by shaking it with 1 N alkali and storing it for a day or so over calcium chloride. The use of isopropyl ether (6) has been discontinued because of the difficulty of keeping it acid-free.

The volumetric glassware should be standardized and all titrations carefully made. No precautions have been taken to exclude carbon dioxide during the titrations.

Summary

The partition method described by Werkman (7) has been used extensively in this laboratory for 5 years and has been modified to meet the demands of fermentation research.

Procedures are given for the determination of the acids in two-acid mixtures by using one partition constant. By the additional use of a second partition constant it is possible to detect the presence of acids other than the two acids assumed to be present. Nomographic methods are used.

The two partition constants may also be used to determine the acids in three-acid mixtures. Procedures are given for the detection of large errors in the analysis of three-acid mixtures by the further use of two additional partition constants.

If formic acid is present in any of the acid mixtures, it is

determined separately and treated as a known quantity. The other acids are determined in the presence of formic acid.

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An Overhead Heater for Rapid Evaporation, Drying, and Charring

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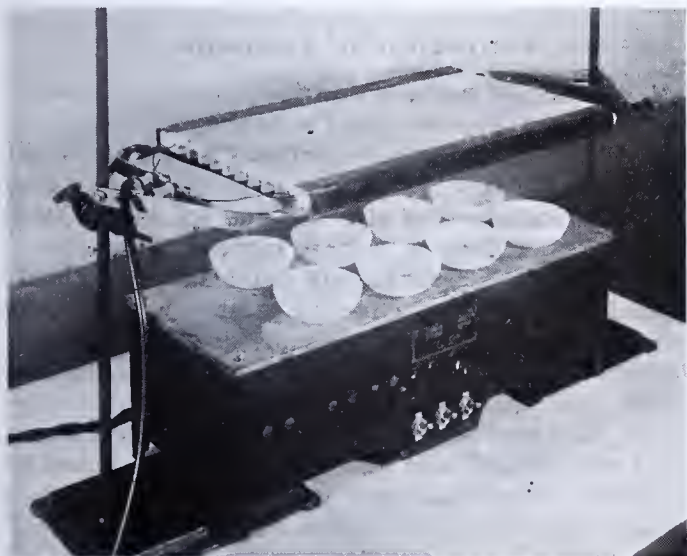


FIGURE 1. RADIANT HEATER AS USED FOR EVAPORATION OF FLUIDS

Hot plate serves only as convenient support for dishes.

THE foaming, spattering, and creeping of fluids that often accompany some of the procedures in quantitative analyses can be obviated by the proper application of heat (1). Figure 1 illustrates a simply constructed overhead heater, made from a standard commercial unit, sufficiently large to allow the simultaneous treatment of ten 50-cc. or four 200-cc. samples. With this apparatus, troublesome evaporations can be carried out expeditiously—for example, 200 cc. of urine can be taken to dryness in half an hour with no signs of ebullition or foaming. Materials such as casein, blood, and sugar, which are difficult to ash by the usual methods, can be quickly dehydrated and charred under the heater. The residues may then be safely placed in a hot muffle furnace to complete the ashing.

The heater is made from the top unit (17.5 × 35 cm., 7 × 14 inches) of a muffle furnace (multiple-unit furnace, Type 56, Hevi Duty Electric Co.), with the radiating face of the unit protected by a sheet of stainless steel (Ka2SMO of the Crucible Steel Co. or equivalent is satisfactory). The apparatus is supported on two ring stands by a suitable brass framework. The heating unit is connected directly to a 220-volt line and draws about 17.5 amperes when hot. Under these conditions the radiating surface becomes a bright cherry red. The amount of heat received by the dishes is regulated by raising or lowering the unit. The efficiency of the radiator could be increased by thermal insulation for the top surface, but it has been found convenient to use the top surface as a high-temperature hot plate. A smaller unit (top unit of a multiple-unit furnace, Type 52), 12.5 × 25 cm. (5 × 10 inches), drawing 10.5 amperes when connected directly to 110 volts, has proved useful for analyzing samples in small crucibles.

In Table I are given the times necessary to complete the procedures there listed. The radiant heater would be especially useful in those methods that require frequent evaporations, such as microdeterminations of bromine or iodine in biological materials, where as much as 24 hours may be saved on a single analysis.

TABLE I. TIME REQUIRED

Material	Operation	Time Min.
Water	Evaporate 200 cc. to dryness	30
Urine	Evaporate 200 cc. to dryness and char	45
Blood	Evaporate 10 cc. to dryness, char, add 1 cc. of coned. nitric acid, and evaporate to dryness	45
Casein	10 grams plus 70 cc. of water and 4 cc. of 8 N potassium carbonate. Evaporate to dryness and char	60
Sodium chloride	0.5 gram plus 2 cc. of coned. sulfuric acid. Evaporate to dryness and heat to cessation of fuming	90
Glucose	10 grams, thoroughly charred	40

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Analysis of Plant Tissue

Application of a Semi-Micro-Kjeldahl Method

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A semi-micromethod, suitable for the determination of nitrogen in plant tissues, is described. The method is rapid, inexpensive, suitable for small samples, and facilitates determination of large numbers of samples. Its precision and accuracy on the basis of a statistical analysis of the data are given.

RESEARCH on the nitrogen metabolism of plant tissues demands a method for accurate determination of total nitrogen on relatively small samples. The limitations imposed on plant culture work—e. g., the necessity for constant environmental and nutrient conditions—do not admit the use of large samples in metabolic studies in which frequent sampling of specific tissues is necessary. Further, as the number of plants in such an experiment is increased the variable factors introduced by varied environmental conditions—e. g., light—play an increasingly important part in determining the extent of growth, and hence results of the experiment. In addition to being applicable to small amounts of material, it is essential that the method be rapid, simple, inexpensive, and adapted to routine determinations on a large number of samples.

This need is most readily met by use of semi-microprocedures. Equal speed and ease of manipulation are possible with microtechnics, but these often require expensive apparatus and specialized skill not always available. In this paper is detailed a semi-micro-Kjeldahl method suitable for plant metabolism studies; this method is essentially a combination of standard procedures used in the macroanalysis, but which have been modified to meet the requirements already outlined. It should be emphasized that semi-micromethods involve more than mere reduction in size of macroprocedures. Methods are too often transferred from macro- to micro- or semi-microtechnic and from one type of tissue to another

without evidence that the method so modified is applicable to the new conditions. Critical examination of macro- and microprocedures for determination of nitrogen have frequently been made, but similar work on semi-micromethods is not available. Moreover, it is fallacious to assume that the existing semi-micromethods developed for the analysis of pure compounds or for animal tissue are suitable for the analysis of plant tissue without some modification. Before acceptance it is essential that evidence be presented concerning the applicability, accuracy, and precision of the modified method when used for routine analysis under given conditions—e. g., in plant metabolism experiments.

Estimation of Ammonia

Of the numerous methods described for the estimation of ammonia, only a few were found to be suitable.

The steam distillation recommended by Parnas and Wagner (6) and distillations of other types, while excellent for micro-work, require considerable attention and are not adapted to routine determinations on a large number of samples. In addition they are not particularly suitable to the estimation of ammonia nitrogen in undigested plant saps. An attempt to simplify the procedure by simple distillation from the semi-micro-Kjeldahl flask through a microdistilling head into standard acid, as in the macromethod, entailed a loss in precision, as is shown by the relatively large standard deviations of the mean (Table I). Aëration into standard acid was found to be satisfactory from the point of view of ease and speed of manipulation, precision, and accuracy. The apparatus used is essentially that of Van Slyke and Cullen (11). A bank of 24 to 36 units is easily operated by a simple water aspirator and the rate of airflow measured with a standardized flowmeter. As will be seen from Table I, the precision and accuracy of this method are entirely satisfactory.

TABLE I. NITROGEN DETERMINATION

Method	Material	Macro-Kjeldahl	No. of Samples	Nitrogen Found (Semi-Micro)
Simple distillation	(NH ₄) ₂ SO ₄	1.94 ± 0.01 ^a	26	1.96 ± 0.05 ^a
		0.97 ± 0.01	25	0.91 ± 0.03
	Digested soybean sap	2.27 ± 0.02	19	2.36 ± 0.03
		0.91 ± 0.02	9	0.99 ± 0.06
Aëration	(NH ₄) ₂ SO ₄	0.39 ± 0.01	3	0.37 ± 0.00
		0.97 ± 0.01	3	0.95 ± 0.01
		1.94 ± 0.01	3	1.94 ± 0.01
	Digested soybean sap	2.27 ± 0.02	30	2.26 ± 0.01
		0.91 ± 0.02	4	0.92 ± 0.00
		0.45 ± 0.02	10	0.46 ± 0.01

^a The deviation given is the standard deviation of the mean.

The rate and time of aëration, the concentration and volume of the sample solution, the temperature, and the pH of the sample, all influence recovery. These factors have been discussed by many workers, particularly Folin (4) and Sessions and Shive (8). By reference to Figure 1 it will be seen that a rate of 1.5 liters per minute at room temperature gives complete recovery in slightly over 3 hours, 4 hours being entirely adequate. Since, longer aëration does not alter the final results, samples may be left aërating as long as is convenient—e. g., overnight—providing the aëration time is at least 4 hours. At aëration rates above 1 liter per minute, addition or omission of inorganic salts does not influence the results. The pH of the sample should be at least 8.0. In aërating from plant juices, excess alkali is to be avoided. For quantities of nitrogen greater than 5 mg. the boric acid absorption of Meeker and Wagner (5) may be used; phenol is somewhat better than boric acid for this absorption. However, in the range from 0.5 to 5.0 mg. of nitrogen the precision of such

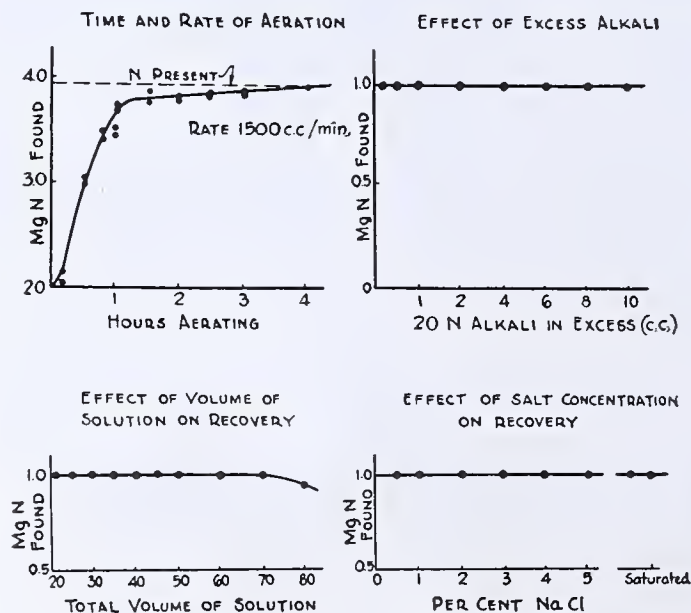


FIGURE 1. EFFECT OF VARIOUS FACTORS ON RECOVERY OF NITROGEN BY AÉRATION

absorptions is not as great as is the 0.018 *N* acid-alkali titration. For smaller quantities of nitrogen the absorption bulbs of Folin (4) are necessary and nesslerization is convenient.

Digestion of Sample

The conversion of nitrogenous compounds into ammonia by digestion with concentrated sulfuric acid in the presence of a catalyst does not always proceed quantitatively and in these cases certain modifications have been introduced. The general method of analysis will be described in detail, then certain modifications indicated for different types of samples.

METHOD FOR TOTAL NITROGEN. The sample, containing from 0.5 to 5.0 mg. of nitrogen, is weighed or pipetted into a 100-cc. semi-micro-Kjeldahl flask and 5 cc. of catalyst-digestion mixture are added. This mixture consists of 2 grams of copper sulfate, 2 grams of selenium oxide, 100 grams of sodium sulfate, 500 cc. of water, and 500 cc. of concentrated sulfuric acid. Modifications to suit specific materials are discussed below. Digestion is carried out over a low flame until almost water-white. For most materials this entire digestion is completed in 30 minutes. The sample is allowed to cool, diluted with about 20 cc. of water, and washed into an aëration tube. The total volume of sample and washing should not exceed 50 cc.

The neutralization of the digestion mixture is carried out in two stages: (1) sufficient 10 *N* alkali is added to change the crystal violet (1 drop of 0.2 per cent solution) from yellow through green to blue (this preliminary addition of alkali is insufficient to cause the evolution of ammonia but accounts for the greater amount of the heat of neutralization). (2) The sample is allowed to cool before making completely alkaline to avoid condensation of moisture in the trap between the sample and receiving tube. This trap may be omitted when the aëration apparatus is used solely for Kjeldahl digest but is necessary in aëration of ammonia from plant juices. The sample tube, then, is cooled, placed in the aëration rack, made entirely alkaline to phenolphthalein, and aërated (1500 cc. per minute) into 25 cc. of 0.018 *N* sulfuric acid for at least 4 hours. The acid is back-titrated with 0.018 *N* sodium hydroxide using bromocresol green.

DRY SAMPLES WITHOUT NITRATE. From 50 to 200 mg. of the sample, ground to 200 mesh, are weighed into the flask, the catalyst-digestion mixture is added, and the samples are analyzed as described above.

DRY SAMPLES CONTAINING NITRATE. The semi-micro salicylic-sulfuric acid analog of the macromethod is entirely applicable. Some slight modifications are necessary, since water must not be added until after nitration and reduction. The sample is weighed as usual, 2.5 cc. of the salicylic-sulfuric acid mixture used in the official macromethod (1) are added, mixed well, and the whole is allowed to stand for 30 minutes. A small crystal of sodium thiosulfate is added and the mixture heated carefully for 5 minutes. After cooling, 5 cc. of modified digestion mixture (exactly the same as the normal digestion mixture except that the 500 cc. of concentrated sulfuric acid are replaced by 500 cc. of water) are added, evaporated until white fumes come off, digested, and aërated as usual. On dry samples containing nitrate the same precision has been found with this modification as with dry samples containing no nitrate.

WET SAMPLES WITHOUT NITRATE. The general method is entirely adequate. The data given in Table I are typical of the results obtained. When plant sap samples are compared with similar samples containing nitrate, both should be run by the nitrate modification, even though one is free from nitrate nitrogen.

WET SAMPLES CONTAINING NITRATE. It has been shown by Ranker (7) that the salicylic acid method is not applicable to wet samples and reduction by other means is necessary. This reduction may be carried out in acid or alkaline solution, the latter being preferable on plant saps in that it eliminates the possible source of error due to the loss of nitrogen from the reaction of nitrous acid on free amino groups present. The method used is that of Davisson and Parsons (2), modified for semi-microwork. The sample is made 0.125 *N* to 0.1 *N* with sodium hydroxide, 150 mg. of Devarda's alloy are roughly measured in, and the flask is attached to the Davisson and Parsons tower, which contains 5 cc. of the normal catalyst-digestion mixture. The flasks are allowed to stand in the cold for about 10 minutes, then warmed slightly until the active evolution of hydrogen ceases (10 to 15 minutes). Foaming may be prevented by adding a drop of capryl alcohol to the sample at the start. The heat is removed and the catalyst allowed to suck back into the flask. With repeated heatings and washings the entire tower

is washed clean and its contents are collected in the flask. Evaporation, digestion, and nitrogen estimation proceed as in the general method. Precision and accuracy are discussed below.

BASIC NITROGEN FRACTION (PHOSPHOTUNGSTIC ACID PRECIPITATES). There is perhaps no group of reduced nitrogenous compounds less susceptible to Kjeldahl nitrogen determination than those found in the fractions precipitated by phosphotungstic acid. Modifications suitable for quantitative determination of total nitrogen in these are discussed by Umbreit and Wilson (10) in connection with the semi-micromethod for basic nitrogen.

Discussion

The precision of the method on various types of samples determined by a comparison of duplicates is fundamental to the interpretation of any results obtained through its use. The method has now been used for over a year in routine analysis on several thousand samples of plant materials, soils, and bacteriological media, as well as in research on nitrogen metabolism. The estimations of precision given in Table II are obtained from the regular routine work of the laboratories now using the method and as such represent the precision under varied conditions of analyst, laboratory, and sample type. The correlation coefficient, *r*, between the nitrogen content of the samples and the difference between duplicates showed these to be independent. The values of *r* given in Table II are not significant as judged by the *t* test (3, 4). The weighted averages of the differences between duplicates are given in Table II; in taking two duplicates from the same sample one can normally expect them to agree within 0.03 or 0.04 mg. of nitrogen, the percentage deviation varying with the nitrogen content (for the 2 mg. of nitrogen range this deviation would be 1.5 to 2.0 per cent of the nitrogen in the sample).

TABLE II. PRECISION OF METHOD

Type of Sample	N Range	Number of Duplicates	<i>r</i>	Weighted Average Difference in Duplicates Mg.
Dry = NO ₃	0.50-4.00	207	+ 0.073	0.031
Wet = NO ₃	0.33-5.28	108	- 0.05	0.041

The accuracy of a method is something apart from its precision, and before the data may be relied upon it must be shown that it is actually determining the component it purports to measure. The method here described gives virtually the same results as does the macro-Kjeldahl method. In those cases where the macro-Kjeldahl disagrees with the Dumas method (9) the results obtained by the use of the semi-micromodification described agree with the macro-Kjeldahl data. The method is therefore subject to the limitations of its macroanalog, though it is not as readily influenced by slight changes in procedure as is the macromethod.

The semi-micromethod is adaptable to all the modifications of the macro-Kjeldahl method. From the data in Table III, it will be seen that in the case of soybean materials, combinations of mercury and hydrogen peroxide with selenium give no better results than selenium alone. Likewise, mercury and hydrogen peroxide alone, permanganate, persulfate, dichromate, phosphoric acid, and copper selenate gave no better results than selenium dioxide with nitrogenous materials from soybeans.

TABLE III. ADAPTABILITY OF METHOD

	(Based on quadruplicate samples of each treatment)				
	Selenium (as SeO ₂)	Selenium + Mercury	Selenium + Hg + H ₂ O ₂	Alkaline Hydrolysis Se + Hg	Selenium
Soybean sap	5.89 ± 0.02	5.84 ± 0.02	5.91 ± 0.02	5.88 ± 0.01	5.90 ± 0.02
Soybean sap	1.79 ± 0.02	1.79 ± 0.03	1.80 ± 0.02	1.80 ± 0.03	1.83 ± 0.02
Basic fraction (soybean)	2.70 ± 0.02	2.72 ± 0.02	2.68 ± 0.02	2.83 ± 0.04	2.87 ± 0.05
Peptone	2.51 ± 0.02	2.52 ± 0.02	2.50 ± 0.02	2.53 ± 0.02	2.55 ± 0.02
Yeast	1.71 ± 0.01	1.81 ± 0.03	1.73 ± 0.01	1.72 ± 0.00

Finally, use of the modifications for nitrate nitrogen in addition to total nitrogen gives quantitative estimation of both forms, as will be noted in Table IV. The authors have found no evidence that the organic matter present is able to reduce the nitrate during the process of digestion, and reduction with nascent hydrogen must be resorted to.

TABLE IV. NITRATE NITROGEN DETERMINATION

Material	No. of Samples	Nitrogen Present Organic ^a	Nitrate	Nitrogen Found		Recovery %
				Total	Nitrate	
		Mg.	Mg.	Mg.	Mg.	
Pure NaNO ₃	6	..	0.45	0.45 ± 0.02	0.45 ± 0.02	100
Sap + NaNO ₃	12	2.25	0.45	2.69 ± 0.06	0.44 ± 0.06	97
Sap + NaNO ₃	5	2.25	0.20	2.45 ± 0.03	0.20 ± 0.03	100

^a Determined on sap before addition of nitrate.

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Determination of Hydroxyl Groups in Organic Compounds

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DURING an investigation of the enzymic synthesis of glycerides it was desirable to have information as to the degree of esterification accomplished at various stages of the reaction. For this purpose a method for the determination of the hydroxyl content of the product, based upon that of Verley and Bölsing (2), was devised. The method of these workers, as originally described, required more material than could be conveniently obtained in the synthetic experiments and, in addition, was not sufficiently rapid. The use of the reagent of Verley and Bölsing—namely, acetic anhydride in pyridine solution—has been applied by other workers to the analysis of small amounts of material [cf. Peterson and West (1), and West, Hoagland, and Curtis (3)], but it seemed possible that some of the precautionary measures, such as the use of condensers and ground-glass stoppers, adopted by these workers to prevent possible losses of reactants might

not be necessary in the analysis of many nonvolatile compounds, especially in view of the fact that the original authors found such measures unnecessary. Moreover, the modified methods were found to be still somewhat time-consuming. Because of the observation that no loss of titratable acid occurs even on fairly vigorous boiling of the acetic acid-pyridine reagent in open vessels without condensers, it has been possible to simplify and shorten the analytical procedure very considerably without loss of accuracy. Before using the method for the purpose for which it was designed it was tested on a number of representative compounds, with the results recorded in Table I.

Experimental Methods

REAGENT. This was a solution of acetic anhydride (either 12 or 20 per cent) in dry pyridine, which was prepared by redis-

TABLE I. HYDROXYL CONTENT OF ORGANIC COMPOUNDS

Compound	—OH Equivalents per Mole, Found	Average	—OH Equivalents per Mole, Theoretical	Error, Per Cent	Source of Compound	Compound	—OH Equivalents per Mole, Found	Average	—OH Equivalents per Mole, Theoretical	Error, Per Cent	Source of Compound
		20 Per Cent Reagent						20 Per Cent Reagent			
1-Naphthol	1.000 1.000 0.995 0.998 0.995 0.997 0.998	0.998	1.000	-0.2	Eastman	Glucose	5.00 4.99 5.00 5.10 5.90 5.83 5.83	5.02	5.00	+0.40	British Drug Houses
Hydroxyisobutyric acid	0.995 0.997 0.998	0.997	1.000	-0.3	Kahlbaum	Mannitol	5.83 5.83 5.89 5.84 5.84 5.85	5.85	6.00	-2.5	British Drug Houses
Salicylic acid	0.999 0.998	0.999	1.000	-0.1	Merck	Sorbitol	5.89 5.84	5.86	6.00	-2.4	Pfanstiehl
Catechol	2.05 1.96 1.93 1.92 2.12	2.00	2.00	0.0	Eastman	Dulcitol	5.84 5.85	5.84	6.00	-2.4	Pfanstiehl
Phloroglucinol	2.99 3.03 3.88 3.98 4.14 3.94 3.90 4.00 4.00	3.01	3.00	+0.33	Eastman	Trichloro-tert-butyl alcohol	0.00	..	1.00	..	Eastman
Arabinose	3.88 3.98 4.14 3.94 3.90 4.00 4.00	3.97	4.00	-0.75	Pfanstiehl	12 Per Cent Reagent					
Xylose	4.18 3.82 4.01 4.13 3.89 3.94 3.94	3.99	4.00	-0.25	Pfanstiehl	Monobutyryl	2.06 1.97 0.35 0.44 0.41	2.02	2.00	+1.0	Schuchardt
						Triolein	1.018 1.004	0.40	0.00	..	Kahlbaum
						Cholesterol	1.018		1.00	+1.8	British Drug Houses
						Oestrone	1.004		1.00	+0.4	Isolated from pregnant mares' urine
						Pregnandiol	1.57 ^a 1.30 ^a 1.96 ^b 1.99 ^b	1.44 1.97	2.00	-28.0 -1.5	Isolated from pregnant human urine

^a Determinations made by the standard method.

^b The reaction mixture, after the preliminary heating, was allowed to stand for 13 hours at room temperature before the final titration.

tilling pyridine which had been dried by refluxing over barium oxide. The 20 per cent reagent is preferred for sugars, whereas either reagent may be used with the other compounds analyzed in the present work.

PROCEDURE. Exactly 2 cc. of reagent are pipetted into a clean dry test tube containing an accurately weighed portion of the substance under analysis, care being taken to wash down with reagent any particles adhering to the side. The weight of the sample varies with the hydroxyl content of the compound—for example, 50 mg. of glucose are sufficient. The mixture is carefully heated over an open flame until the solution boils and for 1 minute longer. After cooling it to room temperature, the solution is diluted with 5 cc. of carbon dioxide-free water and transferred to a small flask; three washings of the tube are made, two with 10-cc. portions of water, and one with 10 cc. of ethyl alcohol. The acid is titrated with 0.1 *N* sodium hydroxide to the cresolphthalein end point. It is necessary, of course, to run blanks for the reagent alone.

In the case of substances containing appreciable proportions of fatty acids which may form difficultly decomposable mixed anhydrides with the reagent it is desirable, after the dilution of the reaction mixture with 5 cc. of carbon dioxide-free water, to boil the solution for 1 minute before finally cooling and titrating. Furthermore, in the analysis of lipoidal substances the final titration is carried out in the presence of sufficient ethyl alcohol to provide a concentration of approximately 50 per cent after the addition of the alkali. Since only one-half of the titratable acid is available for reaction as acetic anhydride, it is desirable, in order to ensure an excess of the anhydride, that three-quarters of the original titratable acidity remain after the completion of the acetylation reaction.

In the analysis of the compounds listed in the second part of Table I the aqueous solution of the reactants was boiled, then cooled, and alcohol was added to the flask before titration. Practically theoretical results were obtained for all compounds listed except the sugar alcohols, the results for

which were about 2.5 per cent low, and the single tertiary alcohol, which did not react. The results for pregnandiol, obtained by the method described, were low; allowing the reaction mixture, after the preliminary heating, to stand overnight (13 hours) at room temperature the results obtained were much closer to the theoretical value. The sample of triolein analyzed was obviously impure, having a deep red color. The method of recording the results tends to emphasize slight errors.

Summary

1. The acetylation method of Verley and Bölsing has been modified to make possible the analysis of small samples of organic compounds.
2. The new method is rapid and convenient and does not require the use of condensers or ground-glass stoppers. It has been applied successfully to representative organic compounds.
3. Tertiary alcohols cannot be estimated by this method.

Acknowledgment

The writers are indebted to G. F. Marrian of this department for the samples of oestrone and pregnandiol used in the investigation.

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Estimation and Identification of the Glucoside Salicin

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A qualitative and quantitative method for the determination of salicin, a glucoside, is presented. The quantitative method depends on the production of a polymerized cleavage product, obtained by acid hydrolysis, which is estimated gravimetrically. A qualitative test which is outlined depends on the solubility of the polymer in a solution of sodium hydroxide with the production of a violet color, and is modified so as to be used as an approximate quantitative colorimetric method. Another qualitative method based on a coupling reaction with *p*-diazobenzenesulfonic acid anhydride is detailed.

THE identification of salicin and its estimation have been studied over a number of years, but the methods obtained by these studies have been long and not easily adapted for accurate work. The importance of glucosides as a class necessitates the development of short and accurate means for

their estimation. The methods in use at present rely on the hydrolysis of salicin either by enzymatic action (?) or by the action of acids (13) and the subsequent estimation of the glucose part of the molecule. None of the methods available are dependent upon the specific chemical nature of salicin, itself, or of the cleavage product, saligenin.

It is well known that when salicin (saligenin- β -glucoside) is hydrolyzed by enzymes or acids, the products are glucose and saligenin. These reactions are noted in Beilstein (3), where it is also noted that saligenin polymerizes on boiling with dilute sulfuric acid to saliretin.

Much work was done by Piria (14), who noted that both salicin and saligenin boiled with dilute hydrochloric acid yielded saliretin. He concluded that saliretin prepared from salicin did not have a definite composition, but prepared from saligenin its formula was C_7H_6O .

Kraut (10) took powdered salicin and ten parts of hydrochloric acid (sp. gr. 1.125), warmed until dissolved, heated to 80° C., and noted the yellowish red color of the resultant saliretin. He concluded that it was saligenosaligenin, $HO \cdot C_6H_4 \cdot CH_2 \cdot O \cdot C_6H_4 \cdot CH_2OH$. On the other hand, von Gerhardt (6) and Beilstein and Seelheim (2) found higher polymers. Kraut also noted that saliretin was soluble in alkalis.

Voswinkel (15) did not obtain the same product from salicin plus hydrochloric acid as with sulfuric acid.

Wischo (17) treated salicin with nitric acid, producing picric acid. He boiled an aqueous solution of salicin with dilute hydrochloric acid, forming saliretin, dissolved the saliretin in potas-

sium hydroxide, and added this solution to the picric acid solution, producing picramic acid and a bluish red color.

Dott (5) gives the following test to identify salicin: To an aqueous solution of the substance to be investigated add two-tenths its volume of hydrochloric acid and warm. The solution develops an aromatic odor and precipitates saliretin. Extract this with ethyl ether and evaporate to dryness. If salicin is present the amorphous residue will be red.

Jackson and Dehn (8) present in tabular form various reactions for the identification not only of salicin but of many other glucosides.

Ware (16) notes that salicin gives a color when warmed with resorcinol and phosphoric or sulfuric acid.

It occurred to the authors that salicin, which has the nature of a phenolic ether, should under the proper conditions couple (1, 11, 12) with a diazonium compound. Salicin does couple with *p*-diazobenzenesulfonic acid anhydride, but only with an alkaline solution prepared from the dry compound.

Qualitative Tests

TEST 1. Dissolve 15 mg. of *p*-diazobenzenesulfonic acid anhydride (4) in 2 cc. of 10 per cent sodium hydroxide solution. Add this to 5 cc. of salicin solution, mix, and place in a warm water bath (approximately 80° C.) for 1 minute. At the end of this time, if salicin is present, a deep red color will develop. Upon the addition of acid the color changes to orange. A very deep red color will be produced by 1 mg. of salicin per cc., and will also develop in the cold, in the case of 10 mg. per cc. at the end of 30 minutes, and in the case of 1 mg. per cc. at the end of 2 hours. It is best to run a blank with the diazonium reagent, in order to be sure that the colors are not due to decomposition of the reagent itself.

This method for the identification of salicin is very simple except for the preparation and keeping qualities of the diazonium reagent. However, at best, it can only be indicative of the presence of this glucoside because of the numerous other substances which will couple with this reagent under exactly the same conditions. The color produced by the reaction between salicin and the diazonium reagent is apparently proportional to the concentration of the former, for the depth of color increases with the concentration of salicin.

TEST 2. Proceed as directed under quantitative colorimetric method, evaporating almost to dryness. A red precipitate soluble in alkali with the production of a violet color, which on dilution becomes salmon-colored, shows the presence of salicin. This color will be produced with as little as 0.2 mg. per cc.

Quantitative Gravimetric Method

The regularity of the changes produced in salicin during evaporation with concentrated hydrochloric acid led to the belief that the production of the precipitate was entirely quantitative.

Place 25 to 50 cc. of the solution to be analyzed containing 1 to 5 mg. of salicin per cc. in a tall-form 100-cc. beaker and add 25 cc. of concentrated hydrochloric acid. Cover with a watch glass on glass hooks and evaporate very slowly on a hot plate carefully regulated to 80° C. or less, down to a volume of not more than 10 cc. Prepare a Gooch crucible or a porous glass crucible with a thin pad of acid-washed asbestos in the usual manner and dry in a constant-temperature oven to constant weight at 100° C. Cool in a desiccator and weigh. Filter the precipitate obtained from the salicin through the Gooch crucible. Carefully transfer all the precipitate to the crucible by means of a rubber policeman and wash bottle. Wash thoroughly with distilled water, suck dry, place in a constant-temperature oven at 100° C., and dry to constant weight. Multiply the weight of the precipitate by the factor 2.524 to obtain the quantity of salicin present in the original aliquot taken for analysis.

Table I gives the results of this method on known quantities of recrystallized salicin.

Acid hydrolysis of salicin conducted as outlined yields results, based on an average recovery of saliretin, which are at least 98.5 per cent accurate. The average deviation from the

mean is 0.006. The method may be applied in the presence of small amounts of lactose, sucrose, inulin, maltose, arabic, tragacanth, karaya, agar, Irish moss, locust kernel, ghatti, starch, and the glucoside amygdalin. These substances do not interfere, for they do not produce a precipitate on evaporation with concentrated hydrochloric acid. Diluted normal urine also does not interfere. On the other hand, the glucosides digitonin and saponin do interfere, for they yield an acid-insoluble precipitate when treated as directed. These precipitates do not have a red color and are insoluble in 10 per cent sodium hydroxide solution. By means of the method given below, salicin may be determined in the presence of these glucosides.

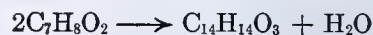
TABLE I. CONVERSION OF SALICIN TO SALIRETIN

Salicin Mg./25-50 cc.	Acid Precipitate Mg.	Ratio of Column 2 to Column 1
39	15.5	0.397
41	16.0	0.390
50	19.0	0.380
50	19.8	0.396
50	20.0	0.400
62.5	24.2	0.387
62.5	24.6	0.394
75	29.2	0.389
75	29.3	0.391
100	39.6	0.396
100	39.8	0.398
125	52.9	0.423
125	49.7	0.398
250	101.2	0.405
250	100.6	0.402
		Mean 0.396

Assuming that salicin splits quantitatively, yielding saligenin and glucose



and that saligenin goes completely to saliretin



then two moles of salicin are equivalent to one mole of saliretin—that is, 572 grams of salicin are equivalent to 230 grams of saliretin. The theoretical yield, if the above holds true, would be 230/572 or 40.21 per cent of salicin used. Table I demonstrates that we recover, expressing the ratio of columns 2 to 1 in percentage, 39.6 per cent of the salicin used, or 98.5 per cent of the theoretical yield. These results indicate that only one polymer of saligenin is formed when conditions of acid hydrolysis are rigidly controlled. Kraut (10), it may be noted, felt that the production of saliretin is quantitative. The factor used in the method is obtained from the reciprocal of the average recovery of saliretin and will, of course, yield the quantity of salicin sought.

Quantitative Colorimetric Method

Place 5 cc. of a solution of salicin containing approximately 1 to 2 mg. per cc. in a 10- to 15-cc. beaker with a mark at 2 cc., add 5 cc. of concentrated hydrochloric acid, and evaporate slowly on a hot plate kept at 80° C. or less to 2 cc. Allow to cool and filter through a small filter. Wash both beaker and filter well with cold water, and replace the receiver of wash water with a tube having a graduation at 10 cc. or with a 10-cc. volumetric flask. Wash beaker and filter paper with 4 successive 1-cc. portions of 10 per cent sodium hydroxide, wash filter once more with 1 cc. of 10 per cent sodium hydroxide, and again wash beaker and filter paper with four successive 1-cc. portions of distilled water. Make receiver tube or volumetric flask up to volume, mix thoroughly, and read in a colorimeter against standard control treated in exactly the same way. The ratio of fourteen determinations comparing unknown to standard had a minimum of 0.925, a maximum of 1.17, and a mean of 1.02 as the variation from unity.

It is obvious that this method has not been completely developed to yield high accuracy; however, the results are of the correct order and are better than some quoted in the

literature (9). Using standard of concentration close to that of unknown would aid in obtaining higher accuracy. This method is far more rapid than others and where interfering substances are present in the gravimetric method, it is better than none. It is at present being studied for better development.

As the hydrolysis of salicin proceeds, the following changes take place: Shortly after the solution reaches a temperature of 80° C., a white turbidity is noticeable. This turbidity changes slowly in an hour or so to a pink precipitate which grows deeper in color as the time of heating and evaporation proceeds. For quantitative conversion, it is essential to evaporate very slowly and at a temperature never higher than 80° C.

The length of time necessary for accurate results indicates that the formation of saliretin proceeds with a definite velocity. The rate of this reaction has never been studied. The concentration of hydrochloric acid is of great importance for, when it falls below a certain minimum, the reaction does not yield quantitative results within a reasonable time.

This work was performed in the Chemical Laboratory of the Bureau of Food and Drugs, Department of Health, City of New York.

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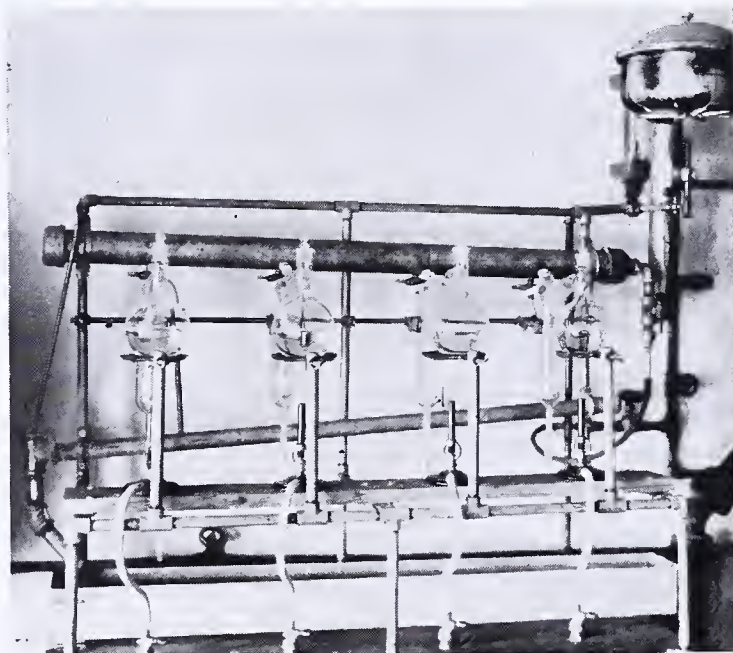
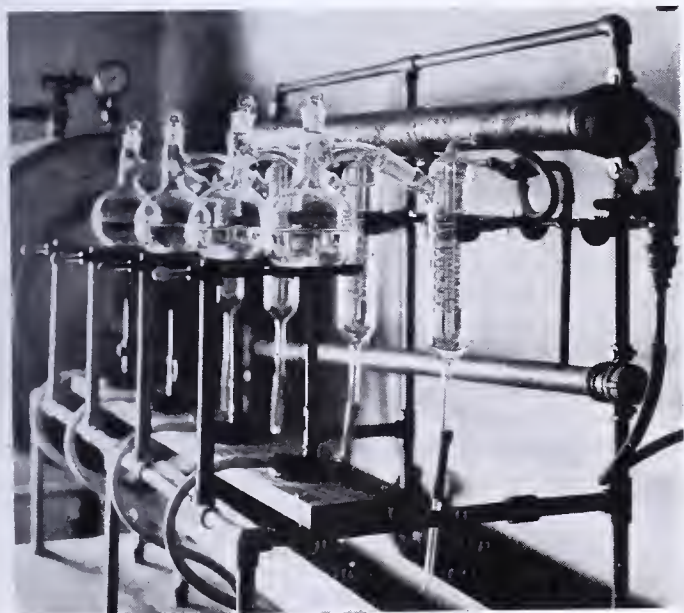
Battery-Type Stand Assembly for Distilling Equipment

ROY L. MOBLEY, P. O. Box 1021, Baton Rouge, La.

THE efficiency of distillation has in many ways been lowered by the equipment available. In the older types of apparatus vapors and liquids were brought in contact with metals, and with cork and rubber joints, stoppers often leaked, and in some instances the units making up the apparatus were inefficient.

The advent of all-glass interchangeable-joint apparatus and improved condensers has brought about much greater efficiency and more accurate results. However, the complete change of type and general form of equipment has made older accessories obsolete, and it is extremely time- and accessory-consuming to set up two or more of the newer types at a time.

In an attempt to overcome these handicaps, the author made the necessary calculations and arrangements, diagrammatic sketches, etc., and developed a working model of a battery-type stand assembly which has proved very satis-



factory during the past 3 years. The photographs show front and diagonal end views of the assembly as built for 500-cc. distilling flasks and indicate arrangement of the parts.

The apparatus was built and used in the laboratory of William L. Owen, Baton Rouge, La.

RECEIVED May 14, 1936.

CORRECTION. In the article on "Determination of Nitric Oxide in Coke-Oven Gas" [*IND. ENG. CHEM., Anal. Ed.*, 8, 164 (1936)] an error was made in Figure 2. The glass balls should be of 5- or 6-mm. diameter, as the 8-mm. balls specified would be entirely too large for this apparatus.

J. A. SHAW

Nomograph for Iodine Value of Tung Oil

C. S. WAN AND K. HO, Chemical Research Laboratory, Government Testing Bureau, Hankow, China

THE iodine value of tung oil as determined by the Wijs method is greatly affected by time of contact, excess of Wijs reagent, and working temperature. These factors have been extensively studied by Ho, Wan, and Wen (1), who have developed the formula

$$\log Y_t = 0.001672 (t + 10.56)(\log X - 2.15) + \frac{2^{(t/10)}}{2^{(t/10)}} \times 0.0008625 + B \quad (1)$$

where

- Y_t = iodine value at working temperature, t
- t = working temperature in ° C.
- X = excess of Wijs reagent in cg. of iodine per gram of oil
- B = characteristic value of individual oil sample

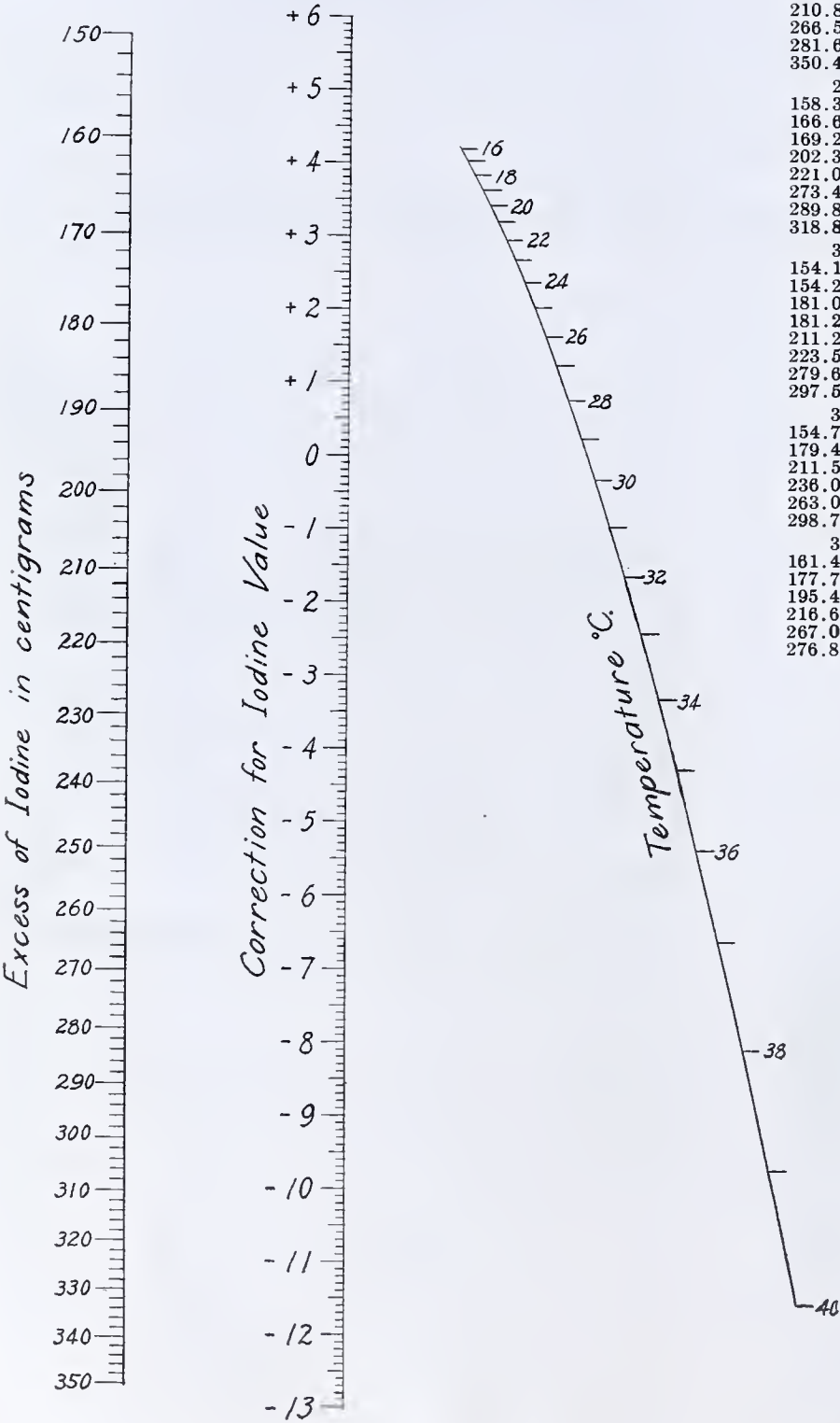


FIGURE 1

TABLE I. COMPARISON OF IODINE VALUES CORRECTED BY NOMOGRAPH AND FORMULA

Experimental Data Excess of iodine, cg./g.	Iodine value	Nomograph Correction	Iodine Value Corrected by Nomograph	Iodine Value Calculated by Formula	Difference
20.0° C.					
160.2	163.6	+3.8	167.4	167.4	0.0
168.2	164.2	+3.4	167.6	167.6	0.0
191.2	165.5	+2.3	167.8	167.8	0.0
218.8	166.5	+1.1	167.6	167.6	0.0
266.8	169.3	-0.6	168.7	168.7	0.0
270.0	169.0	-0.7	168.3	168.3	0.0
333.4	169.9	-2.5	167.4	167.4	0.0
350.0	171.3	-2.9	168.4	168.4	0.0
26.3° C.					
169.0	165.2	+2.3	167.5	167.5	0.0
183.7	167.0	+1.4	168.4	168.4	0.0
208.3	167.2	+0.1	167.3	167.3	0.0
210.8	167.8	0.0	167.8	167.8	0.0
266.5	170.5	-2.4	168.1	168.1	0.0
281.6	171.1	-3.0	168.1	168.1	0.0
350.4	172.4	-5.3	167.1	167.1	0.0
29.2° C.					
158.3	165.4	+2.4	167.8	167.8	0.0
166.6	166.1	+1.8	167.9	167.9	0.0
169.2	166.2	+1.7	167.9	167.9	0.0
202.3	168.0	-0.3	167.7	167.7	0.0
221.0	169.0	-1.3	167.7	167.7	0.0
273.4	171.8	-3.7	168.1	168.0	+0.1
289.8	172.3	-4.4	167.9	167.9	0.0
318.8	173.3	-5.4	167.9	167.8	+0.1
32.0° C.					
154.1	165.1	+2.1	167.2	167.2	0.0
154.2	165.5	+2.1	167.6	167.6	0.0
181.0	167.0	+0.2	167.2	167.2	0.0
181.2	167.6	+0.2	167.8	167.8	0.0
211.2	168.7	-1.7	167.0	167.1	-0.1
223.5	170.1	-2.4	167.7	167.7	0.0
279.6	172.0	-5.1	166.9	166.9	0.0
297.5	173.1	-5.8	167.3	167.3	0.0
35.6° C.					
154.7	167.3	+1.1	168.4	168.4	0.0
179.4	169.0	-0.8	168.2	168.2	0.0
211.5	170.3	-3.0	167.3	167.3	0.0
236.0	173.1	-4.4	168.7	168.7	0.0
263.0	173.6	-5.9	167.7	167.7	0.0
298.7	176.0	-7.6	168.4	168.4	0.0
38.6° C.					
161.4	168.2	-0.5	167.7	167.7	0.0
177.7	169.6	-1.8	167.8	167.8	0.0
195.4	170.8	-3.2	167.6	167.7	-0.1
216.6	171.9	-4.6	167.3	167.3	0.0
267.0	175.7	-7.6	168.1	168.1	0.0
276.8	175.8	-8.1	167.7	167.7	0.0

In order that the iodine values of tung oil determined in different laboratories can be readily compared, they have proposed to use 250 cg. excess of iodine and a time of contact of 1 hour at 20° C. as common standard conditions. Under the proposed standard conditions, Equation 1 is simplified as follows:

$$\log Y = 0.0161 + B \quad (2)$$

where

- Y = iodine value at proposed standard conditions
- B = characteristic value of individual oil sample

Before making use of Equation 2, one has to calculate the value of B by means of Equation 1. The calculation, though not very difficult, is rather complicated and requires much time.

The authors, after carefully studying the relations, have worked out a nomograph, from which one can read off the correction and consequently obtain the iodine value at the proposed standard conditions without going through comprehensive calculation.

If a straight line is drawn from a particular excess of iodine and working temperature of the experiment, it will intersect the correction scale. When the correction indicated on this scale is applied to the iodine value obtained experimentally under laboratory conditions, one gets directly the iodine value at 250 cg. excess of iodine and 20° C. It is understood that the time of contact is to be exactly 1 hour.

Example

Oil taken, 0.1505 gram
Sodium thiosulfate in blank titration, 46.86 cc.
Sodium thiosulfate used for the test, 26.61 cc.
Difference, 20.25 cc.
Strength of sodium thiosulfate solution, 1.264 cg. of iodine per cc.
Experimental iodine value, $\frac{20.25}{0.1505} \times 1.264 = 170.1$
Excess of iodine, $170.1 \times \frac{26.61}{20.25} = 223.5$ cg. of iodine per gram of oil

Working temperature, 32° C.
Time of contact in the dark, 1 hour
When 223.5 on the excess scale and 32 on the temperature scale in the nomograph are joined by a straight line, the line will intersect the correction scale at -2.36. The iodine value at the proposed standard conditions is then equal to 170.1 - 2.36, or 167.7, which checks very well with the value calculated by the formula.

The authors have carefully checked the data contained in their previous article (1). The iodine value calculated with their formula and those read off from this nomograph are tabulated together in Table I for comparison.

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RECEIVED February 20, 1936. Published with the permission of C. Y. Wang, Commissioner of Government Testing Bureau, Ministry of Industry, Hankow, China.

Quantitative Determination of 5-Methyl Furfural

HAROLD A. IDDLES AND KENDRICK S. FRENCH, University of New Hampshire, Durham, N. H.

IN THE production of furfural by the distillation of various pentose- and pentosan-containing natural products with mineral acids, it would be expected that any methyl pentoses and methyl pentosans would yield 5-methyl furfural in an analogous manner and the polysaccharides which hydrolyze to hexoses would give rise to small amounts of μ -hydroxy 5-methyl furfural.

The effect of these compounds, particularly 5-methyl furfural, on the quantitative determination of furfural was first studied by Votoček (18), who prepared a pure sample of 5-methyl furfural from rhamnose, with which precipitations with phloroglucinol were carried on to determine the ratio of product to aldehyde employed. Later Ellet and Tollens (5) studied the relation between the quantity of phloroglucinol precipitate and the amount of rhamnose employed as a test sample in hydrochloric acid distillation. Fromherz (6) determined the furfural and methyl furfural in samples of wood by the production of the phloroglucides with a subsequent attempted separation of the mixed precipitate by using the alcohol solubility of the phloroglucides of 5-methyl furfural. Dox and Plaisance (3) questioned the reliability of this alcohol separation of the phloroglucides and recorded in their work the qualitative reaction of thiobarbituric acid with 5-methyl furfural but gave no quantitative data because of the limited amount of material on hand.

Since it is now possible to prepare pure 5-methyl furfural in quantity according to the directions of Rinkes (14), it seemed desirable to make a comparative study of the various gravimetric and volumetric methods for the determination of furfural when applied to pure 5-methyl furfural itself. In this direct study it is possible to eliminate the variables introduced when the calculations refer back to an original methyl pentose or methyl pentosan sample which has undergone an acid distillation. The methods selected for study were the phloroglucinol or A. O. A. C. method (1), the thiobarbituric acid method (3, 10, 17, 19), the 2, 4-dinitrophenylhydrazine method (8, 16), the volumetric bromide-bromate titration method (2, 4, 10-13, 15), and the volumetric bromide-bromate titration at 0° C. (7).

Preparation of 5-Methyl Furfural

The 5-methyl furfural was prepared according to the method of Rinkes (14) in which levulose, produced by acid hydrolysis of sucrose, is dehydrated to produce μ -chloro-5-methyl furfural and the chlorine is replaced by hydrogen

by means of stannous chloride reduction. The resulting product was vacuum-distilled at 75° to 76° C. and 13 mm. pressure, yielding clear samples for analysis which showed a n_D (Pulfrich) of 1.53049 at 20° C., and 1.52643 at 25° C.

Gravimetric Methods

PHLOROGLUCINOL METHOD AND METHOD OF CALCULATION. In the procedure as finally developed, a weighed sample of the pure redistilled 5-methyl furfural was diluted to 1 liter with distilled water and 5-, 10-, or 15-ml. aliquot portions were drawn from a buret into 200 ml. of 12 per cent hydrochloric acid solution. To this was added 0.33 gram of phloroglucinol in 50 ml. of 12 per cent hydrochloric acid solution, a quantity which is in excess of the amount necessary for the 5-methyl furfural present. After waiting 8 to 10 minutes for precipitation to begin, the solution was diluted to 400 ml. using 12 per cent hydrochloric acid and allowed to stand 16 to 20 hours in the dark. Finally the precipitate was collected on a tared Gooch crucible, washed with 150 ml. of cold water, and then dried in a vacuum desiccator over a dehydrating agent to prevent the darkening and decomposition caused by drying in the oven at 100° C., which is the practice with furfural.

In the work of Fromherz (6) the ratio of the weight of precipitate to the weight of sample increased with the size of sample used. To substantiate these results, a series of determinations was made, using samples varying from 0.018 to 0.132 gram to determine the effect of sample size on the ratio of precipitate to sample.

TABLE I. EFFECT OF SAMPLE SIZE ON RATIO OF PRECIPITATE TO SAMPLE

Weight of Sample Gram	Weight of Precipitate Gram	Weight of Precipitate Weight of Sample
0.0180	0.0182	1.012
0.0226	0.0270	1.194
0.0265	0.0345	1.302
0.0451	0.0745	1.652
0.0529	0.0897	1.696
0.0541	0.0917	1.696
0.0677	0.1201	1.774
0.0794	0.1468	1.849
0.0902	0.1686	1.869
0.1058	0.2019	1.905

It can be seen from Table I that the ratio tends to increase regularly with the size of sample from 1.012 to 1.905. This increase may be explained by considering the solubility of precipitate to remain constant in the constant volume of

TABLE II. GRAVIMETRIC DATA

Methyl Furfural Used	Pre-cipitant Used	Pre-cipitate	Methyl Furfural Found	Methyl Furfural Recovered	
Gram	Gram	Gram	Gram	1 ^a	2 ^b
				%	%
Phloroglucinol Method					
0.0180	0.33	0.0182	0.0182 ^c	82.2	101.2
0.0180	0.33	0.0184	0.0183	83.0	101.7
0.0180	0.33	0.0179	0.0181	81.3	100.4
0.0226	0.33	0.0267	0.0223	85.2	98.6
0.0226	0.33	0.0272	0.0225	86.4	99.6
0.0226	0.33	0.0270	0.0224	86.0	99.2
0.0451	0.33	0.0750	0.0454	99.2	100.6
0.0451	0.33	0.0741	0.0449	98.2	99.6
0.0451	0.33	0.0746	0.0452	98.6	100.2
0.0529	0.33	0.0897	0.0524	99.1	99.0
0.0529	0.33	0.0902	0.0526	99.6	99.5
0.0529	0.33	0.0893	0.0522	98.8	98.7
0.0677	0.33	0.1194	0.0666	100.5	98.4
0.0677	0.33	0.1203	0.0670	101.2	99.0
0.0677	0.33	0.1210	0.0674	101.6	99.5
0.0794	0.33	0.1475	0.0800	104.5	100.8
0.0794	0.33	0.1462	0.0794	103.9	100.0
0.0794	0.33	0.1424	0.0776	101.0	97.7
0.0902	0.33	0.1684	0.0900	104.0	99.8
0.0902	0.33	0.1688	0.0902	104.1	100.0
0.0902	0.33	0.1686	0.0901	104.1	99.9
0.1058	0.33	0.2024	0.1063	105.9	100.4
0.1058	0.33	0.2017	0.1059	105.2	100.1
0.1058	0.33	0.2016	0.1059	105.2	100.1
0.1322	0.33	0.2542	0.1310	105.4	99.0
0.1322	0.33	0.2564	0.1321	105.9	99.8
0.1322	0.33	0.2547	0.1314	105.5	99.3
			Av.	98.0	99.7
Thiobarbituric Acid Method					
0.0206	0.15	0.0434	0.0202	98.1	
0.0206	0.15	0.0431	0.0201	97.6	
0.0206	0.15	0.0444	0.0207	100.5	
0.0237	0.15	0.0508	0.0237	100.0	
0.0237	0.15	0.0507	0.0236	99.6	
0.0237	0.15	0.0503	0.0234	98.7	
0.0411	0.15	0.0875	0.0408	99.3	
0.0411	0.15	0.0866	0.0404	98.3	
0.0411	0.15	0.0886	0.0413	100.5	
0.0474	0.15	0.1015	0.0473	99.8	
0.0474	0.15	0.1011	0.0471	99.4	
0.0616	0.15	0.1321	0.0616	100.0	
0.0616	0.15	0.1327	0.0619	100.5	
0.0616	0.15	0.1331	0.0621	100.8	
0.0711	0.15	0.1511	0.0704	99.0	
0.0711	0.15	0.1502	0.0700	98.5	
0.0711	0.15	0.1534	0.0715	100.8	
			Av.	99.5	
2,4-Dinitrophenylhydrazine Method					
	Ml.				
0.0110	50	0.0294	0.0112	101.7	
0.0110	50	0.0294	0.0112	101.7	
0.0110	50	0.0293	0.0111	100.9	
0.0162	50	0.0430	0.0163	100.6	
0.0162	50	0.0430	0.0163	100.6	
0.0162	50	0.0432	0.0164	101.2	
0.0221	50	0.0582	0.0221	100.0	
0.0221	50	0.0589	0.0223	100.9	
0.0324	50	0.0861	0.0327	100.9	
0.0324	50	0.0860	0.0326	100.6	
0.0486	50	0.1282	0.0486	100.0	
0.0486	50	0.1282	0.0486	100.0	
			Av.	100.8	

^a Calculated by formula $W = 1/1.9 (Ph + n \times 0.000018)$.
^b Calculated by formula from curve $W = 0.4780 (Ph + 0.0199)$.
^c Methyl furfural found by phloroglucinol method calculated as in ^b.

solution, so that the effect would be proportionately greater in the cases of small samples. To allow for this solubility factor a formula was devised which could be used to calculate the weight of 5-methyl furfural from the weight of phloroglucide precipitate. The weight of precipitate was plotted against the weight of sample used (Figure 1), giving a curve which is a straight line. The curve does not pass through the origin but would cross the abscissa on which the phloroglucide was plotted at a point corresponding to -0.0199 gram. If the weight of precipitate is increased by 0.0199 gram for each sample, the resulting curve would be parallel to the first, and would pass through the origin. By taking the slope of the curve in Figure 1 the following formula was obtained:

$$W = 0.4780 (Ph + 0.0199)$$

where W is the weight of sample used, Ph is the weight of phloroglucide precipitate, and 0.0199 is the correction factor

to account for the solubility of precipitate, together with any other factors which may tend to lower the yield of precipitate when working under the specified conditions in a constant volume of 400 ml.

Using this formula to calculate the results in Table II, satisfactory agreement is obtained between the values of sample taken and found, the average error being 0.2 mg. and the maximum, 2 mg. in thirty analyses. The earlier formula of Fromherz (6), $W = 1/1.9 (Ph + n \times 0.000018)$, where n = volume of solution in ml., gives satisfactory calculated values only in the region of 0.06-gram samples. For smaller samples the calculated values are low and for larger ones the results are high, the amounts computed by the Fromherz formula rising steadily from about 82 to 106 per cent of the 5-methyl furfural actually used in the authors' experiments.

THIOBARBITURIC ACID METHOD. To a sample of pure methyl furfural, diluted to 200 ml. with 12 per cent hydrochloric acid, was added the precipitant consisting of 0.15 gram of thiobarbituric acid, slightly in excess of the equivalent amount, also dissolved in 12 per cent hydrochloric acid. After precipitation had commenced, the final volume was made up to 400 ml. with 12 per cent hydrochloric acid and allowed to stand for 2 days to ensure complete precipitation.

The methyl furfural thiobarbiturate precipitated very slowly but was more dense and filtered more easily than the corresponding furfural precipitate. The weight of methyl furfural was calculated on the basis of a reaction ratio of one molecule of 5-methyl furfural to one of thiobarbituric acid, using the conversion factor 0.4660. The results which are given in Table II show a very close agreement between the actual weight of sample taken and the amount calculated from the precipitate by use of the above theoretical conversion factor. The average error is about 0.2 mg. and the maximum about 1 mg.

2,4-DINITROPHENYLHYDRAZINE METHOD. A measured sample of the aqueous solution containing a weighed quantity of 5-methyl furfural was added dropwise to 50 ml. of a saturated 2 *N* hydrochloric acid solution of 2,4-dinitrophenylhydrazine. The hydrazone which formed as a granular red precipitate was allowed to stand for 1 hour at 0° C. in an ice bath, and was then filtered, washed with 2 *N* hydrochloric acid and water, and finally dried over phosphorus pentoxide in a partial vacuum. From the weight of the dried hydrazone, the weight of 5-methyl furfural may be calculated, using the factor 0.3793. The results recorded in Table II show that the error of the method is generally less than 0.2 mg.

Volumetric Methods

VOLUMETRIC POTASSIUM BROMATE-BROMIDE METHOD. Following the method suggested by Powell and Whittaker (13) for furfural, 25-ml. portions of approximately 0.1 *N* potassium bromate-bromide (0.132 *N* actually used), were pipetted into four glass-stoppered flasks. To two of these the samples of 5-methyl furfural made up to 200 ml. with 12 per cent hydrochloric acid were added, and to the other two, 200 ml. of 12 per cent hydrochloric acid were added for blank runs. After standing for 1 hour in the dark, 10 ml. of 10 per cent potassium iodide were added and the liberated iodine was titrated with 0.10038 *N* sodium thiosulfate. The number of milliliters of standard sodium thiosulfate required by the sample subtracted from the number required for the blank was a measure of the bromine consumed by the 5-methyl furfural.

Whereas the addition of bromine to furfural takes place to the extent of 4.05 atoms per molecule of furfural, which is an empirical value under carefully controlled conditions, the results in Table III indicate that 5-methyl furfural was more active in the addition of bromine than furfural, so that approximately 5 atoms of bromine were added for each molecule of 5-methyl furfural. Using varying sized samples with the same quantity of reagent, the addition of bromine proceeded further in the cases of smaller samples during the reaction period of 1 hour. Since this effect may be caused by the proportionally larger concentration of bromine, as stated by Hughes and Acree (7), three samples were run

containing 0.0275, 0.0551, and 0.0826 gram to which 24, 34, and 43 ml. of potassium bromate-bromide mixture were added, respectively, so that the excess of bromine would be nearly the same in each case. The results obtained correspond to 5.02, 4.99, and 4.97 atoms of bromine and were more nearly constant at 5 atoms for the varying sized samples of 5-methyl furfural. The increase in bromine consumption with 5-methyl furfural to approximately 5 atoms, whereas furfural used 4.05 atoms, may be due to an increase in chemical reactivity toward bromine, as well as possible temperature effects in these experiments, for Magistad (12) and Hughes and Acree (7) have observed large temperature coefficients for these brominations in the case of furfural.

TABLE III. ADDITION OF BROMINE TO FURFURAL

Weight of Sample Gram	Ml. of 0.10038 N Na ₂ S ₂ O ₃ for Blank Less Ml. for Sample	Atoms of Br per Mole of Methyl Furfural
0.0303	13.75	5.017
0.0303	13.95	5.090
0.0303	13.80	5.036
0.0448	20.53	5.017
0.0448	20.48	5.054
0.0448	20.53	5.017
0.0448	20.48	5.054
0.0605	26.70	4.872
0.0605	26.70	4.872
0.0605	26.75	4.881
0.0605	26.80	4.890
0.0672	29.23	4.808
0.0672	29.12	4.788
0.0672	29.30	4.820
0.0672	29.41	4.838

VOLUMETRIC POTASSIUM BROMATE-BROMIDE TITRATION AT 0° C. The method of Hughes and Acree (7) differs from the foregoing in that 3 per cent hydrochloric acid is used and the temperature is maintained at 0° C. which reduces the addition of bromine to furfural to exactly 2 atoms per molecule of furfural. In the case of furfural the present authors obtained very satisfactory results but, in using exactly the same procedure, the greater reactivity of 5-methyl furfural made it impossible to hold the addition to exactly two atomic proportions of bromine but instead much higher and erratic addition values were obtained.

Comparison of Methods

In this study quantitative precipitation of 5-methyl furfural was obtained by using each of the three reagents phloroglucinol, thiobarbituric acid, and 2,4-dinitrophenylhydrazine, under conditions which are adjusted carefully while the volumetric potassium bromate-bromide methods did not yield satisfactory results, employing conditions outlined in this work. In the case of the phloroglucinol method, it was necessary to carry on the precipitation in a definite volume; to prevent decomposition of the precipitate during the drying process; and to weigh the precipitate rapidly, since it was hygroscopic. When a solubility correction factor was applied, recovery values showed a maximum error of less than 2 mg. with an average error of 0.2 mg. for the complete series of determinations. The thiobarbituric acid method gave a more stable precipitate which offered no trouble in drying and weighing. The results showed a maximum error of 1 mg. with an average error for the seventeen recorded samples of 0.2 mg. The use of 2,4-dinitrophenylhydrazine as a precipitant gave the most rapid precipitation and the most consistent results, showing a maximum error of 0.3 mg. and an average error of 0.13 mg.

In applying the volumetric methods, the reaction with bromine has been shown to take place much more readily with 5-methyl furfural than with furfural and seemed to vary with the concentration of bromine and the quantity of sample to be determined. Consequently this method is not suitable

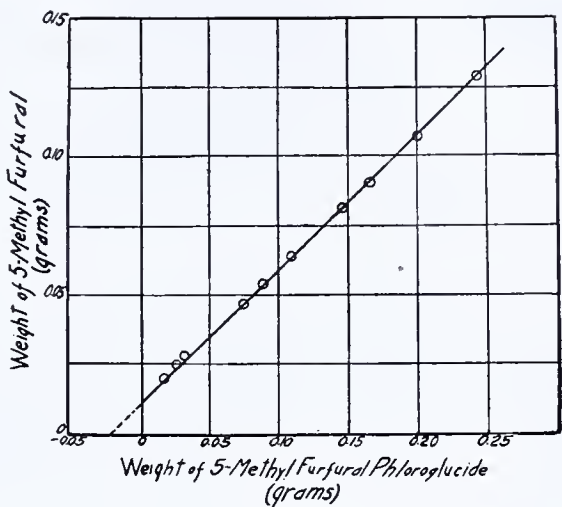


FIGURE 1. PRECIPITATION CURVE

for the determination of varying sized samples of unknown, since the amount of potassium bromate-bromide solution to be used would depend on the size of sample to be titrated. In the work on the determination of furfural in woods by one of the authors (9), higher results for furfural in the distillate were reported for the volumetric method than in the phloroglucinol gravimetric method. Since some 5-methyl furfural is undoubtedly produced from hard woods, it seems that the slightly higher results may be due to the increased reaction of bromine with the 5-methyl furfural present.

Conclusions

1. Phloroglucinol has been used to determine 5-methyl furfural by introducing an empirical correction factor for solubility of the phloroglucide precipitate. In calculating the 5-methyl furfural from the phloroglucide the formula $W = 0.4780 (Ph + 0.0199)$ was found to be more satisfactory than the formula used by Fromherz, $W = 1/1.9 (Ph + n \times 0.000018)$.
2. 5-Methyl furfural precipitates quantitatively with either thiobarbituric acid or more satisfactorily with 2,4-dinitrophenylhydrazine.
3. The use of the potassium bromate-bromide titration procedure at room temperature or at 0° C. does not yield quantitative results under the conditions used in analogous furfural determinations.

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Micromethod for Determining Boiling Points of Liquids at Different Pressures

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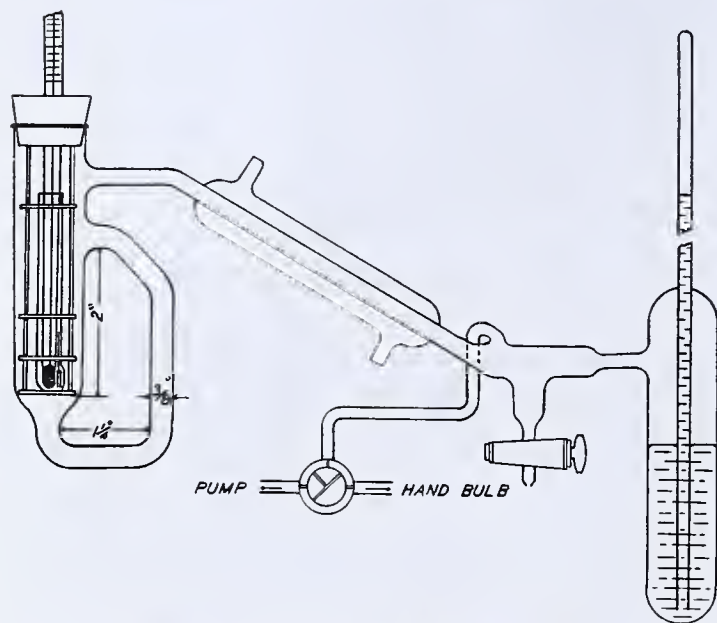


FIGURE 1. DIAGRAM OF APPARATUS

LABORATORIES located at altitudes other than sea level have difficulty with courses in qualitative organic analysis because in standard reference works boiling points of most organic compounds are given only for sea-level conditions. This has been the experience in Denver, where the barometric pressure varies between 623 and 631 mm.

The authors have been successful in designing an apparatus for obtaining boiling points for pressures between 900 and 10 mm. with sufficient accuracy for the purposes of qualitative organic analysis. Figure 1 shows the design of the apparatus used.

A small test tube 9 by 70 mm., containing a few drops of the liquid to be tested, is enclosed in a closed system in which the

pressure may be varied and observed. A small capillary tube sealed about 7 mm. from the open end is placed in the liquid. The authors have found it convenient to blow a slight bulge near the bottom of the tube for the capillary tube to rest in. The bulb of the thermometer is immersed in the liquid in the test tube, which is surrounded by a system of brass baffle plates as shown. This baffle system has been found to be very important if accurate results are to be obtained. The bottom baffle plate holds the test tube in place.

The pressure is increased by use of a small baumanometer bulb and low pressures may be obtained in any convenient fashion. Pressures are read on the mercury barometer on a meter stick, which is adjustable by means of a screw. The bath is heated until there is a rapid evolution of bubbles at the pressure desired, and then allowed to cool. The temperature at which the liquid starts to rise in the capillary tube is taken as the boiling point. As soon as this temperature is reached the pressure and temperature are recorded. The pressure is then reduced about 10 cm. immediately, causing a further rapid evolution of bubbles. The liquid is again allowed to cool until the liquid rises in the capillary tube and the temperature and pressure are again noted. In this way a vapor pressure curve may be obtained in a very short time.

Figure 2 shows the vapor pressure curve for water as determined and as given in the literature. Table I records boiling points for sea level as determined at Denver for ten common organic liquids, together with boiling points recorded by Kamm (1). The boiling point of ethyl oxalate at 10 mm. is also included. All the temperatures are uncorrected.

TABLE I. BOILING POINT DETERMINATIONS

Compound	Experimental ° C.	Literature ° C.	Pressure Mm.
Ethyl iodide	72.5	72	760
n-Amyl alcohol	137	137	760
Methyl acetate	57	57	760
n-Butyl carbonate	206.5	205	760
Ethyl acetate	77	77	760
n-Amyl chloride	108.2	108	760
o-Chlorophenol	174.5	175	760
Ethyl carbonate	126.5	126.0	760
Carbon disulfide	47	46	760
Chloroform	61.6	61	760
Diethyl oxalate	75	72-74	10

The bath liquids in Table II have been found suitable for the indicated temperatures and pressures.

TABLE II. BATH LIQUIDS

	Maximum Temperature ° C.	Pressure Mm. Hg
Mineral oil (Squibb's)	150	10
	260	760
Glycerol	150	20
	250	760

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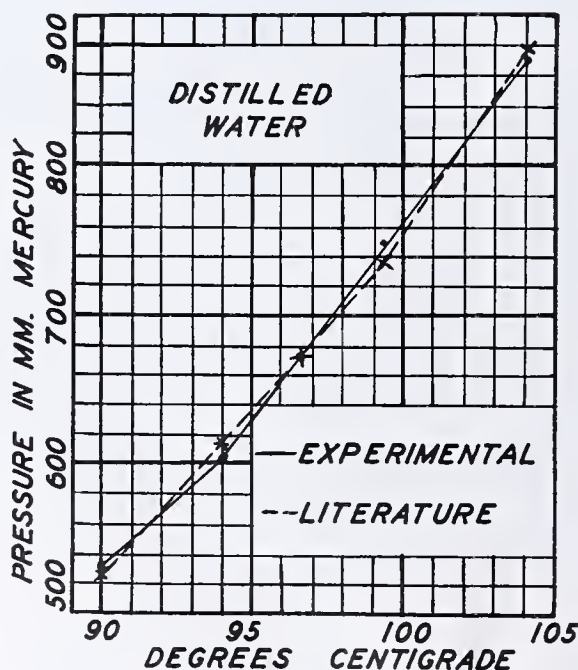


FIGURE 2. VAPOR-PRESSURE CURVE



Determination of Acidity in Insulating Oil

Use of the Glass Electrode in *n*-Butanol

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This paper outlines a potentiometric method for the titration of acids in oil in which the glass electrode in *n*-butanol is employed. The need for a small amount of water in the solvent is pointed out. Fac-

tors relating to the titration procedure are dealt with experimentally. The effect of easily hydrolyzable substances on the shape of the titration curve and on the estimation of acidity of oils is discussed.

THE usefulness of an electrical oil may be more accurately determined if one attempts to estimate the deleterious substances in the oil by more refined chemical procedures. Thus, in the past, a great deal of work has been done in attempting to correlate electrical and chemical test results, with little or no success because of lack of refinement in chemical test procedures together with an incomplete interpretation of the significance of the test data actually obtained. For example, it is rarely emphasized that such substances as metal soaps and peroxides may be included in the simple neutralization number test, although the effect of the latter substances on the electrical and chemical properties of the oil far outweighs the effect of the elementary acid group carboxyl. Inasmuch as the work herein reported is a result of a study of the deterioration of high-voltage cable oil in particular, the procedure for acidity determination must of necessity be capable of revealing small amounts of acids—i. e., a neutralization number of 0.01 or less.

The value of the glass electrode (3, 6) in aqueous solutions is well known under conditions which militate against the use of hydrogen, quinhydrone, or analogous substances to stabilize the potential. Similar objections may be raised to the use of these substances in non-aqueous solvents. Although the authors have found that the presence of water in the titration medium is essential for the precise determination of acidity in oil with the glass electrode, it will be necessary to modify the apparatus considerably to connect the activity of the water in the solvent definitely to the behavior of the

glass electrode. Thus, since small amounts of water are involved, the entire operation must be carried out in the absence of air. This phenomenon is the subject of further study.

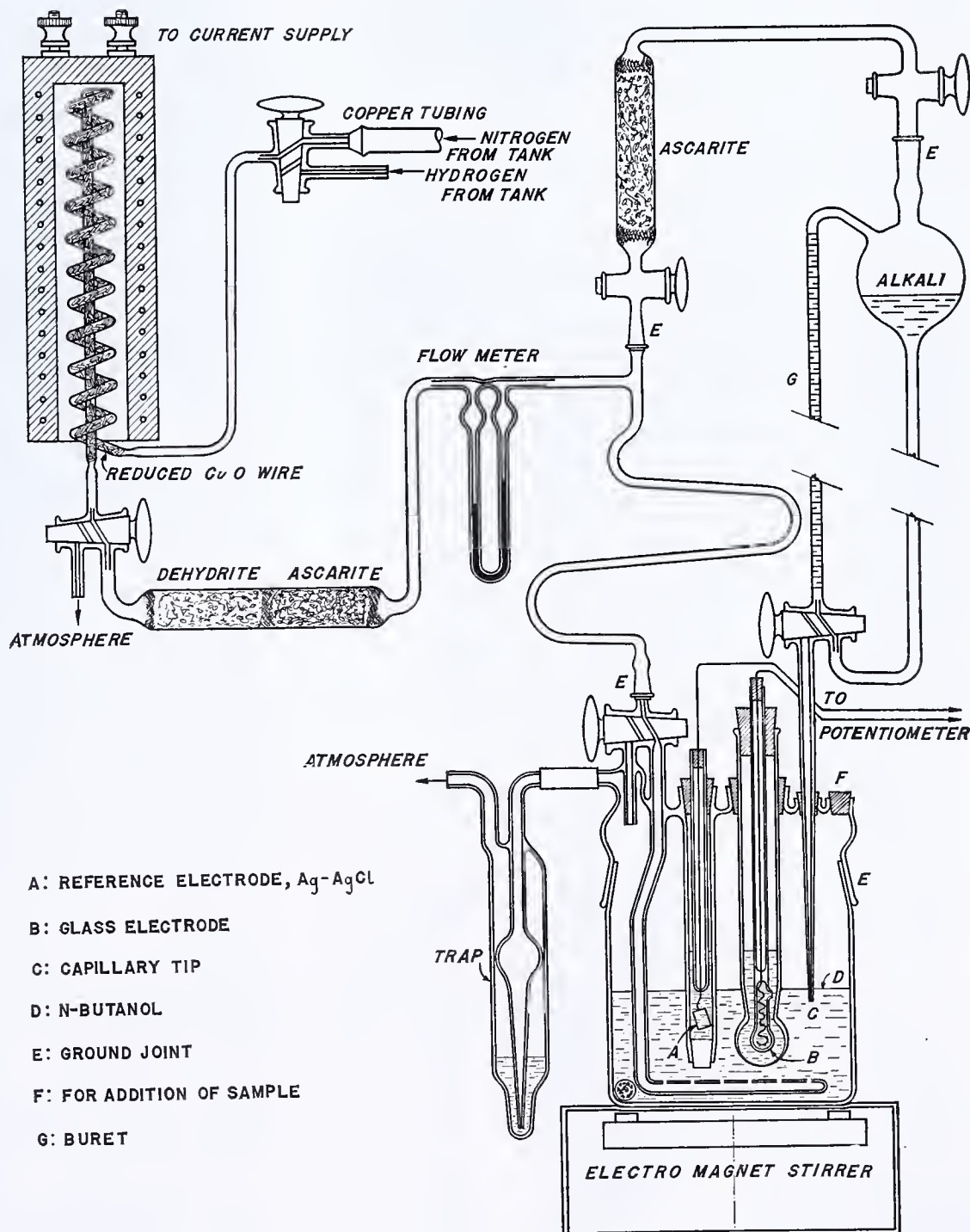


FIGURE 1. DIAGRAM OF TITRATION APPARATUS

from the solvent by the nitrogen was surprisingly large—1.00 to 1.2 cc. of 0.01 *M* alkali per 100 cc. of *n*-butanol which had been distilled without protection from air contamination. The magnetic stirrer was operated during the entire gassing period.

ALKALI. The most stable solvent for the alkali was anhydrous methanol prepared by distillation from sodium. Potassium hydroxide was dissolved in the alcohol, forming a concentrated solution. Separation of the insoluble carbonate was effected by centrifuging and an aliquot part was pipetted and added to the alcohol which had been distilled into the alkali storage reservoir. The resulting alcoholic potassium hydroxide was 0.01 *M*, as measured by titration of strong (hydrochloric, picric) or weak (benzoic, stearic) acids. In other words, the weak acid salt content (14) of the alkali was too small to be detected and remained so for several months (Figure 3). *n*-Butanol containing potassium hydroxide was found to be more susceptible to oxidation and light action, although it was satisfactory for use in oil acidity titrations.

Experimental Results

The general applicability of the present experimental setup in its use for oil acidity determinations is discussed and illustrated below.

VOLATILE ACIDITY AND STANDARDIZATION. It is possible to measure volatile as well as nonvolatile acidity. The problem of volatility of acids becomes particularly important where small amounts of acids are being determined. The use of an inert gas for agitation in conjunction with any electrode pair is open to serious criticism unless some precaution is taken to eliminate the loss of volatile acid. Furthermore, the solvent becomes quickly contaminated with volatile acid upon exposure to the atmosphere either before or during the titration period. The removal of the volatile acid is illustrated in Table I, where 100 cc. of *n*-butanol were employed as a solvent for 1 cc. of 0.005 *M* stearic acid in toluene.

TABLE I. REMOVAL OF VOLATILE ACIDITY FROM *n*-BUTANOL BY MEANS OF NITROGEN

(Gas flow approximately 1 cc. per second)

0.01 <i>M</i> KOH Equivalent to Residual Acid in Solvent Cc.	Time of Gassing Min.
0.14	20
0.10	30
0.06	60

As the volatile acid was more completely removed by the longer gassing period the point of inflection of the stearic acid became more distinct. The oil sample should be obtained under conditions which prevent atmospheric contamination whenever an inert atmosphere is employed to protect the oil during its life as a dielectric.

The alkali standardization curves are given in Figure 3.

Curve A shows the titration of Bureau of Standards benzoic acid, alkali 0.0097 *M*. The molarity of the alkali employing recrystallized picric acid was 0.0096. Curve B represents the titration of a mixture of 2 cc. of 0.0053 *M* hydrochloric in methanol and 1 cc. of 0.0052 *M* stearic acid in toluene. The difference in titers is 0.63 cc. which is the titer obtained with 1 cc. of 0.0052 *M* stearic acid alone (curve C). The addition of 1 cc. of 0.0052 *M* stearic acid to the excess alkali from curve C followed by titration gave 0.55 cc. as the titer of the 1-cc. portion of stearic acid. It follows that the residual acidity of the solvent was 0.08 1 cc. of 0.0 *M* alkali. The stearic acid, which probably contained some palmitic acid, was not used as a standard, but merely to prove the absence of weak acid salt in the alkali and to determine the residual acidity in the solvent.

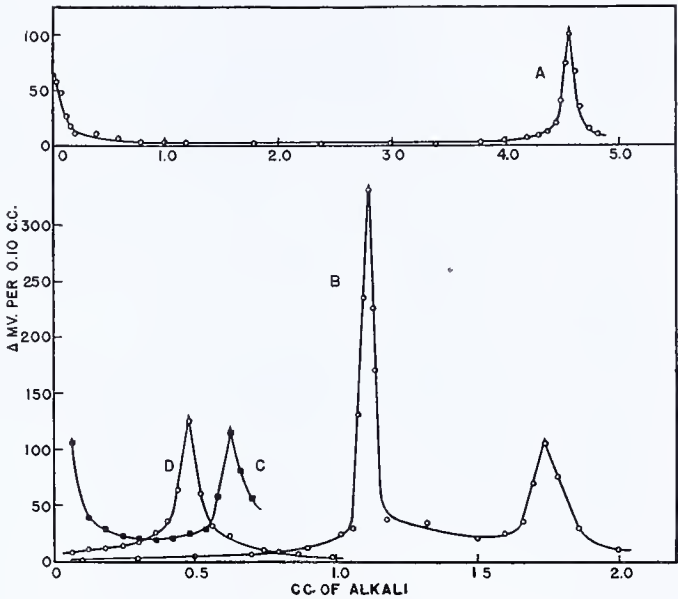


FIGURE 3. STANDARDIZATION OF 0.0097 *M* ALKALI

- A. Titration of benzoic acid, 5.4 mg. Titer, 4.55 cc.
- B. 1 cc. of 0.0052 *M* stearic acid and 2 cc. of 0.0053 *M* hydrochloric acid. Titrers, 1.11 and 1.74 cc.
- C. 1 cc. of 0.0052 *M* stearic acid. Titer, 0.63 cc.
- D. Addition of 1 cc. of 0.0052 *M* stearic acid to excess alkali resulting from C. Titer, 1.18 cc.

ALKALI TO ACID TITRATIONS. The electrode system enables one to proceed from acid to alkali or in the reverse direction. It is thus suitable for saponification experiments.

In Figure 4 curve A shows the titration of 0.9 cc. of 0.01 *M* stearic acid in 100 cc. of *n*-butanol, free of volatile acids but containing the equivalent of 0.15 cc. of 0.01 *M* alkali residual acidity. When 2.2 cc. of alkali had been added, the solution was back-titrated with 0.01 *M* stearic acid in methanol, which is shown in curve B. Curve C illustrates the titration of excess acidity resulting from curve B. Curve C differs from curve A in that the rapid change in potential upon the first addition of alkali is absent. This phenomenon is normally observed in the titration of weak acids in aqueous solutions.

The agreement between acid and alkali is satisfactory considering that 0.10-cc. increments were added. It is obvious that for the saponification test an excess of stearic acid may be added to the residual alkali and titrated in the usual manner. Apparently, the drift in potential at the equivalent point is small as indicated by the relation between acid and alkali independent of the direction of neutralization.

PEROXIDES. The use of quinhydrone with oils that contain peroxides should be questioned. When using the glass electrode no quinhydrone and conducting salt are necessary in the titration medium (2, 4, 10, 11, 12). However, peroxides present an unavoidable difficulty, in that they are attacked

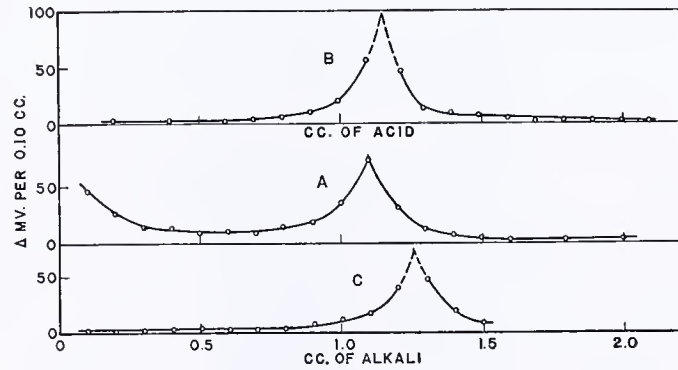


FIGURE 4. ALKALI TO ACID TITRATION

- A. Titration of 0.9 cc. of 0.01 *M* stearic acid. Blank, 0.15 cc. 0.95 cc. of alkali = 0.90 cc. of acid
- B. Back-titration of excess alkali from A with 0.01 *M* stearic acid. 1.10 cc. of alkali = 1.15 cc. of acid
- C. Titration of excess stearic acid. 1.15 cc. of alkali = 1.10 cc. of acid

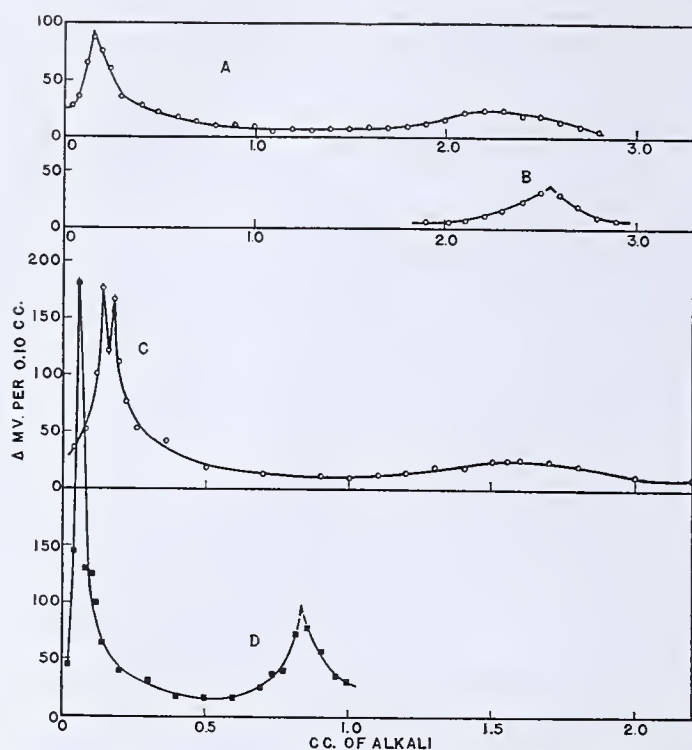


FIGURE 5. EFFECT OF PEROXIDES ON TITRATION CURVE

- A. 15 grams of cable oil, peroxide No. 45, after removal of volatile compounds by means of nitrogen
- B. Titration of excess alkali from A after addition of 1 cc. of 0.01 *M* stearic acid
- C. 9 grams of cable oil, peroxide No. 0. Soluble copper, 7 p. p. m. Volatile constituents not removed
- D. 18 grams of cable oil, peroxide No. 1.5. Volatile constituents absent

by the alkali in the region of the weak acid point of inflection. This effect brings about a flattening in the region of inflection and thus may render the end point obscure. Figure 5, curve A, represents the titration of a commonly used high-voltage cable oil with a peroxide number of 45 after exposure for 48 hours to ultraviolet light. Addition of stearic acid at the end of the titration, followed by a second titration, gave a somewhat more distinct point of inflection (Figure 5, curve B). The oil sample in Figure 5, curve D, had a peroxide number of 1.5. The peroxide number of the oil was obtained by the method of Yule and Wilson (15) and is defined in the authors' work as the grams of active oxygen per thousand kilograms of oil. In general an oil with a high peroxide number presented an obscure end point upon titration, independent of its volatile acid content. There appeared to be no stoichiometrical relation between the peroxide number of the oil and the magnitude of the flattened portion of the titration curve. When benzoyl peroxide was added to the titration medium containing the stearic acid, it was impossible to obtain a point of inflection. In the region of the end point, after addition of alkali, the potential drift would reverse after its normal change due to the alkali and there would follow a slow drift in potential in the acid direction.

It must not be assumed that peroxides were the sole contributing cause to the difficulty discussed in the previous paragraph. Any functional group which reacts with alkali would bring about the same effect. In curve C, Figure 5, the oil sample contained 7 p. p. m. of soluble copper but possessed a peroxide number of approximately zero. The manner in which certain copper soaps interfere with oil acidity determinations is discussed below.

The question naturally arises as to just where the point of equivalence between acid and alkali should be taken when interfering substances are present. The cell potential is of some aid, but even if an arbitrary potential were chosen the difficulty could not be overcome. Consideration of the relation between acid and alkali would call for a point of equivalence

in curve A, Figure 5, immediately above the peak in curve B—a point on curve A which would never have been taken as the end point. Obviously, the alkali was combining with substances which were not present as acids in the original oil sample. Until the exact relation between alkali and the easily hydrolyzable substances in the oil sample is known, the difficulty will remain unsolved.

ACID STRENGTH. One can distinguish between strong and weak acids in the oil sample—a result which in general can be obtained with any electrode pair. Curve C, Figure 5, represents the formation of strong acid in cable oil in the presence of oxygen and finely divided copper. The second point of inflection may represent a moderately strong acid but most probably the hydrolysis of a copper salt of a strong acid. Curve D, Figure 5, shows the formation of acids in a duplicate sample of cable oil in the absence of copper, but under the same oxygen pressure.

COPPER SOAPS. The use of quinhydrone in the presence of aqueous copper sulfate solutions has been investigated by O'Sullivan (8). He reported the slow formation of a precipitate when quinhydrone was used in a neutral copper sulfate solution, bringing about a gradual drift in potential. The use of the glass electrode eliminated this possible interference when titrating insulating oils, which frequently contained copper colloiddally dispersed in the elementary state or combined as soaps. However, the estimation of acids in electrical oils was unavoidably complicated by the fact that certain soaps hydrolyze so easily that they behave as acids when titrated potentiometrically. Thus, a mixture of copper stearate recrystallized from *n*-butanol and stearic acid (curve A, Figure 6) gave but one point of inflection and a titer equivalent to the sum of the two constituents was obtained. Copper cyclohexane carboxylate recrystallized from *n*-butanol (curve B, Figure 6) behaved in a similar manner. The potentiometric determination of soaps is the subject of a paper which will be submitted in the near future.

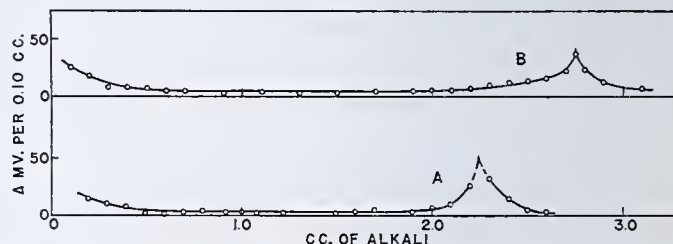


FIGURE 6. EFFECT OF COPPER SOAPS ON TITRATION CURVE

- A. Titration of mixture of 3.2 mg. of copper stearate and 3 mg. of stearic acid. Theory, 2.14 cc.; found, 2.25 cc.; blank, 0.15 cc.
- B. Titration of mixture of 3.35 mg. of copper cyclohexane carboxylate and 1 cc. of 0.005 *M* stearic acid. Theory, 2.73 cc.; found, 2.75 cc.; blank, 0.05 cc.

Conclusions

It is difficult to state definitely the precision with which acidity in oils may be determined with the procedure outlined in this paper. Oils from different sources obviously contain variable amounts of peroxides, metal soaps, and weak acids of different strengths—factors which tend to render the anticipated point of inflection for the oil sample indefinite. When interfering substances are absent—a case which practically reduces to the determination of two solvent blanks—the precision of the method is ± 0.02 cc. of 0.01 *M* alkali. For a 20-gram sample of oil, this amount of alkali is equivalent to a neutralization number of ± 0.001 .

Acknowledgment

The authors wish to express their appreciation of the assistance of Ward F. Davidson, director of research, particu-

larly for the design and construction of the vacuum-tube potentiometer.

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Energy Equivalents of Vitamin D Units

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THE widespread acceptance of irradiated food products and irradiated ergosterol, as well as the general use of cod liver oil and its concentrates, has demanded the formulation of unitary expressions of vitamin D activity. In this country the Steenbock unit, prior to the acceptance of the International unit by the U. S. Pharmacopœia, had received widespread use. The Steenbock unit was originally defined in terms of the amount of calcium deposited in a standard rachitic rat under standard feeding conditions in 10 days. A reference preparation of irradiated ergosterol of known potency expressed in such units was made available for use in other laboratories.

At the time of the adoption of the International unit by the Permanent Commission on Biological Standardization of the League of Nations in 1931, the authors immediately initiated experiments comparing the Steenbock unit with the International unit. Their initial experiments were of the therapeutic type. Preliminary experiments necessitating certain comparisons revealed provisionally that 1 Steenbock unit was equivalent approximately to 2.7 International units. This factor was sufficiently accurate for the purpose at that time (7). Unfortunately, it was accepted by others as the final conversion factor for purposes requiring a far greater degree of accuracy than demanded by the authors' particular experiments.

A limited number of quantitative studies relevant to the amount of energy required to synthesize vitamin D from ergosterol have been reported (2, 4, 5), and their results are generally concordant in showing that within certain limits there exists a definite relation between the amount of radiant energy absorbed and the amount of vitamin D synthesized. The authors have now used a similar technic to determine the amount of radiant energy required to synthesize one International unit of vitamin D in comparison with the Steenbock unit, using ergosterol as the substrate.

Experimental

Known amounts of radiant energy of known wave lengths were obtained with the use of a Bausch and Lomb quartz monochromator equipped with a Coblenz linear thermopile (12 copper-Constantan junctions) in conjunction with a Leeds & Northrup galvanometer (sensitivity, 10.4 mm. per mv.). The thermopile-galvanometer system was standardized with a carbon filament lamp obtained from the U. S. Bureau of Standards. The instrument was adapted for the purpose by the insertion of a quartz lens with a focal length of 5 cm. between the exit slit and the thermopile. This made it possible to place in front of the thermopile slit a cell, 2.5 cm. wide and 1.5 cm. thick, consisting of two compartments constructed of ground and polished plates of quartz. A rack provided for this cell en-

abled the authors to move either compartment into the path of the monochromatic radiations incident to the thermopile slit, thereby eliminating reflection and absorption by the quartz and the solvent as factors in the quantitative evaluations. As a source of light the authors used a capillary quartz mercury arc similar to one described by Daniels and Heidt (1). The degree of resolution of the spectrum from this arc as well as the energy values of different lines is shown in Figure 1. It is evident that the dispersion was sufficient for the purpose.

In their first quantitative evaluations of the Steenbock unit the authors irradiated ergosterol in absolute alcohol solution with the 303 μ mercury line. (The ergosterol was obtained from Chas. Pfizer and Co. It had a melting point of 158° C., uncorrected, a rotation of $(\alpha)_D^{20} = -134.3^\circ$ in chloroform, and an extinction coefficient of 11,000 at 282 mm.) Five cubic centimeters of a 0.1 per cent solution were placed in one compartment of the cell and 5 cc. of absolute alcohol in the other. The cell was sealed with a glass plate and placed on the rack in front of the thermopile slit. Readings of the galvanometer deflections for the determination of the energy transmitted by the absolute alcohol were made before and after the irradiation period for these short exposures. Since the radiant energy incident to the ergosterol solution was all absorbed, this measurement represented the radiant energy absorbed. The amperage and voltage of the arc were always checked. Each solution after proper exposure to measured amounts of radiant energy, ranging from 500 to 5000 ergs, was fed in oil to rats using the 10-day line test technic with ration 2965 as the rachitogenic diet.

Earlier results indicated that healing comparable to that produced by one Steenbock unit was obtained when 3000

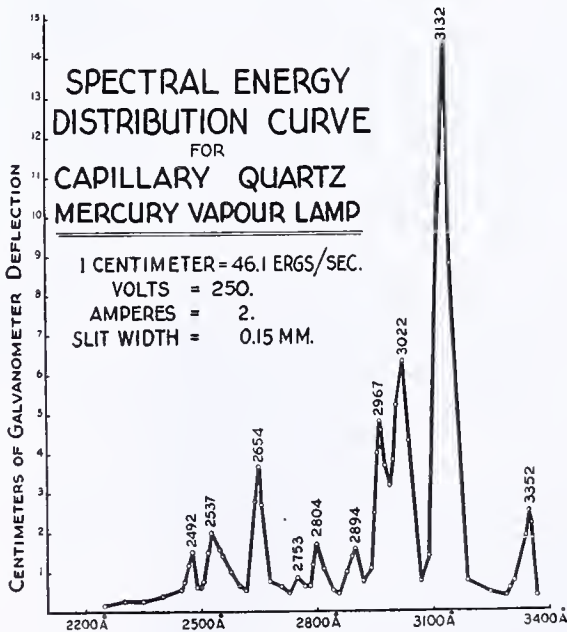


FIGURE 1

ergs of radiant energy of wave length 303 μ were absorbed by the ergosterol solutions. These experiments have been repeated, using the following prominent lines of the mercury vapor arc: 249, 254, 265, 275, 280, 289, 297, 303, and 313 μ . All of them with the exception of the 313 μ line were found essentially equally effective per unit of energy absorbed.

Kon, Daniels, and Steenbock (4), using the line test, and Marshall and Knudson (5), using roentgenograms as criteria, have reported that within the synthesizing region the quantum efficiency was identical for the various wave lengths. The authors' results represent an approximate 20 per cent difference in the number of quanta required to produce one Steenbock unit with the 248 μ line as compared with the 303 μ line. However, this difference may not be based on actual differences in potency, because of the limited accuracy of the line test with the animals used at that time. The authors have, however, repeatedly determined differences of 15 per cent in vitamin D activity, using the prophylactic method with 6 to 10 animals in each group of a series. The daily administration of as little as 0.025 Steenbock unit per day for 5 weeks produces a demonstrable response. One-tenth Steenbock unit per day, or a total of 3.5 Steenbock units for the experimental period of 5 weeks, has been found to be sufficient to protect a rat against rickets on rachitogenic diet 2965.

To determine more accurately the relative effectiveness of the various wave lengths in the synthesizing region the authors repeated their irradiation with the various lines of the mercury vapor arc and fed the resultant preparations in oil to rats in prophylactic experiments with bone ash determinations as the criteria. The results of these experiments are presented in Table I, series 1 and 2. They confirm the results of previous therapeutic studies that the amount of vitamin D produced is proportional to the amount of radiant energy absorbed and independent of the wave length within a considerable range. It also confirms the fact that the upper limit of the ultraviolet zone capable of synthesizing vitamin D lies between 303 and 313 μ . Hess and Anderson (3) reported in 1927 that the longest wave length producing antirachitic activity was 313 μ .

TABLE I. EFFECTIVENESS OF VARIOUS WAVE LENGTHS
(Ash of femurs from rats fed daily the amount of vitamin D produced by 150 ergs of various wave lengths)

	Wave Length μ	Number of Rats	Average Gain in Weight	Average Ash	
			Grams	Gram	%
Series 1	249	6	43	0.0504	40.55
	265	6	41	0.0481	40.06
	289	6	36	0.0522	40.62
	302	6	43	0.0499	39.49
	313	6	42	0.0321	29.64
	Negative controls	6	36	0.0253	26.11
Series 2	254	6	38	0.0617	47.04
	265	6	31	0.0606	45.64
	275	6	39	0.0523	43.74
	280	6	38	0.0579	44.78
	297	6	33	0.0501	43.81
	Negative controls	6	33	0.0292	29.46

The energy relations which the authors have expressed were obtained under rigidly controlled experimental conditions. It is to be expected that the energy relationship, 3000 ergs = 1 Steenbock unit, will not hold when the course of the reaction has proceeded to the point where the rate of destruction of the vitamin is greater than the rate of synthesis. However, the authors have found that the relationship still holds when 10⁴ ergs have been absorbed by 1 mg. of ergosterol in absolute alcohol. Their evaluations were made when approximately 10³ ergs had been absorbed.

They have also determined the amount of radiant energy required to synthesize one International unit of vitamin D

from ergosterol in absolute alcohol solution. To make this determination they exposed an ergosterol solution to a measured amount of radiant energy of wave length 265 μ . This preparation was diluted so that the daily dose of vitamin D was expressed in terms of radiant energy absorbed. Five dilutions were made and compared with the International standard preparation using rats in prophylactic experiments.

From the data presented in Table II it is apparent that 0.165 International unit daily produced a somewhat greater deposition of ash than the daily intake of vitamin D produced by 140 ergs of radiant energy. The energy required to produce an International unit was, therefore, slightly greater than 850 ergs. It appears permissible to conclude that one International unit is equivalent to the vitamin D produced by 900 ergs of radiant energy of wave length 265 μ .

TABLE II. DETERMINATION OF RADIANT ENERGY REQUIRED TO PRODUCE ONE INTERNATIONAL UNIT

Preparation	Ergs per Day	Number of Rats	Average Gain in Weight	Average Ash	
			Grams	Gram	%
119A. Irradiated ergosterol	115	10	62	0.0407	34.80
119B. Irradiated ergosterol	140	10	53	0.0419	35.77
119C. Irradiated ergosterol	165	10	57	0.0451	37.94
119D. Irradiated ergosterol	190	10	58	0.0484	39.78
121A. International standard preparation	0.165 International unit	13	50	0.0412	35.97

From the authors' data in the energy equivalents of one Steenbock unit it is obvious that it requires approximately 3.33 times as much radiant energy to produce one Steenbock unit as one International unit.

TABLE III. COMPARISON OF STEENBOCK AND INTERNATIONAL UNITS

(Percentage of ash produced by 0.025 Steenbock unit per day as compared with that produced by different amounts of the International standard)

	Vitamin D Intake per Day	Number of Rats	Average Gain in Weight	Average Ash	
			Grams	Gram	%
Series 1	Steenbock unit				
	0.025	12	35	0.0395	37.91
	International unit				
	0.0475	12	36	0.0316	32.36
	0.0575	12	33	0.0309	31.85
	0.0675	11	30	0.0298	32.89
	0.0775	12	30	0.0337	36.76
	0.0875	12	30	0.0423	40.32
Series 2	0	10	26	0.0246	27.44
	Steenbock unit				
	0.025	10	48	0.0376	35.60
	International unit				
	0.0825	11	42	0.0356	35.63
	0	12	29	0.0240	26.66

The ratio of the two units to each other which the authors established from their energy evaluations with independently executed biological tests has been checked by direct comparative biological tests. They prepared a standard preparation of known vitamin D activity expressed in Steenbock units with monochromatic light of wave length 265 μ , using essentially the same technic as already described. This preparation was fed in oil from a calibrated dropper to rats at a level of 0.025 Steenbock unit per day. Similarly, the International standard preparation as obtained from the Health Organization of the League of Nations was fed at daily levels of 0.0475, 0.0575, 0.0675, and 0.0875 International unit. From the resultant data, presented in Table III, series 1, it is evident that the number of International units required to produce an ash equivalent to that produced by 0.025 Steenbock unit lies between 0.0775 and 0.0875 International unit. As this was too wide a range, another series of animals was fed 0.0825 International unit and 0.025

Steenbock unit daily. The results of this series, presented in Table III, series 2, show that the response obtained with these two preparations was identical. As the dosages of 0.025 to 0.0825 are in the ratio of 1 to 3.33, the results confirm the ratio obtained in the previous series. (Russel and Taylor, 6, have reported, while this manuscript was being prepared, that one Steenbock unit is equivalent to 3.2 International units.)

Summary

1. One International unit of vitamin D was synthesized from ergosterol when 900 ergs of ultraviolet energy within the synthesizing region were absorbed. Similarly, one Steenbock unit was synthesized when 3000 ergs were absorbed. These values were found to be independent of the wave length within the synthesizing region.

2. A comparison of the energy equivalents of the two units, as obtained in independently executed series of assays, and direct comparison of the biological potency of the International Standard Preparation with a preparation produced

by a measured amount of monochromatic ultraviolet revealed that one Steenbock unit of vitamin D is equivalent to 3.33 International units.

Acknowledgment

The authors acknowledge their indebtedness to Farrington Daniels for helpful counsel in the experimental work.

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The Smoke Tendency of Refined Kerosene and Its Determination

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BEFORE the present century, kerosene was not so well refined as it is now, various types of crude oils being used for its manufacture, often without segregation. The product sold varied widely in such characteristics as viscosity, capillarity, boiling range, and sulfur content, all of which are now closely controlled. The researches of Edeleanu were of inestimable value in showing that the aromatic hydrocarbons, which are removed from the crude kerosene by his well-known sulfur dioxide process, were responsible to a large extent for smoky flames, the removal of such compounds resulting in much larger flames having greater luminosity.

Even though much better grades of kerosene have been marketed during the last 25 or 30 years, it is only within the last 15 years that attention has been paid to the quality of kerosene as judged by its tendency to smoke (1, 4, 7, 8, 9). Burning tests have been devised and standardized with a view to determining oil consumption, wick incrustation, chimney fouling, and luminosity (candle power), all of which have produced very enlightening and indispensable information concerning quality.

Oils are usually tested in lamps of varying design, depending on the particular purpose for which the oil is to be used. Lamps for such burning tests are not well adapted for smoke tendency tests because chimneys and flames differ in shape and size, so that grading of the oil is rendered difficult; large round wicks 2 or 3 inches in diameter, which are very susceptible to "pitting," are often used; a considerable personal element is introduced; it is difficult, using such lamps, to grade oils to detect small differences in refinement; and test lamps of the same type are apt to vary when made by different manufacturers, so that an oil may burn with a different efficiency in two supposedly similar lamps.

Development of Smoke Tendency Tests

In recent years, investigations of the chemical constitution of kerosenes of different degrees of refinement have shown that the constitution of any kerosene is closely related to its tendency to smoke in a given lamp. This is well illustrated

by the work of Minchin (5, 6) who states that the tendency to smoke is directly proportional to its aromatic or naphthene content. In the case of homologous series, the tendency to smoke, with the exception of the paraffins, decreases with the increase in the number of carbon atoms or boiling point. The naphthene class has a flame height about three times that of the aromatic, and the paraffin about nine times that of the aromatic.

Jackson (3) has further pointed out that a satisfactory test for smoke tendency gives all we need to know for test purposes regarding the percentages of aromatics, naphthenes, and paraffins present in the kerosene. Therefore, a reliable test for smoke tendency would be of great value in controlling the burning qualities of illuminating oils. On the basis of experimental work done in England, the Institution of Petroleum Technologists has standardized on a smoke point test for kerosene (2), I. P. T. Serial Designation K.36.

Davis Factor Lamp

In the United States, similar experimental work has been proceeding for more than 10 years. One of the earliest lamps to be developed was the Davis factor lamp (Figure 1), designed in 1923 by R. F. Davis of the Standard Oil Company of California. The basis of its design was that as increased refinement enables a given kerosene to burn with a higher flame in any one lamp without smoking, a lamp which produced a long narrow flame would be adaptable for control of refinement. The tall flame would be sensitive to oils differing by small increments of refining, and the heights of such a flame could be accurately read and would give a good index of quality.

The original design of this lamp included a brass fount of approximately 4-ounce capacity, and regulating wick gears actuated by a larger milled wheel. A special cylindrical glass chimney 7 inches long, 1 inch in outside diameter, and graduated in tenths of an inch was mounted on a brass screen which allowed entrance of air to the flame. In making a determination, the flame was turned up until a "tail" of smoke just appeared. The flame was then slowly turned down until this tail just disappeared,



FIGURE 1. DAVIS FACTOR LAMP

the height of the flame being read on the chimney and recorded. A Handlam long-time-burning felt wick, 0.25 inch in diameter, was used. This lamp gave fairly reliable results, though not entirely satisfactory, and later modifications were made.

Improved Factor Lamp

The improved factor lamp (Figure 2) consists of the following: **BRASS FOUNT**, approximately 4-ounce capacity. Regulating wick gears are enclosed in the brass housing.

BRASS SCREEN, 20-mesh, allows entrance of air at the base of the flame.

CHIMNEY, 7 inches long made from uniform glass tubing, 1 inch outside diameter and 0.03 to 0.06 inch in thickness. A chimney holder maintains the chimney in a vertical position.

SCALE, made of aluminum, 4 inches long and graduated in 0.1-inch divisions, mounted at the side of the burner. It is adjusted so that the zero mark on the scale coincides with the top of the wick tube.

WICK TUBE, round, 0.25 inch in diameter.

WICK, American Pett, 0.25 inch in diameter.

ASSEMBLY. The lamp is placed on the base of a regular ring stand, on the vertical rod of which is mounted a ring which moves freely in a horizontal position and is actuated by means of a control rod. The ring supports a 3-inch flat-bottomed porcelain dish filled with cracked ice for detecting the smoke point. Both the control rod for the ring and the milled operating wheel to adjust the flame height are extended through the right side of a ventilated cabinet fitted with a glass front door. This enables the lamp to be operated in a draft-free space, and allows operating controls to be manipulated from without.

Procedure

The oil to be tested is placed in the fount and filled within 0.5 inch from the top. A piece of wick approximately 4 inches long is cut, placed in the burner, and burned so that the tip is rounded on the top and no rough edges remain. The burner and wick assembly is then placed in the fount, and the chimney set in place, care being taken that the flame is burning centrally within the chimney. The porcelain dish with a clean undersurface is filled with cracked ice and placed in the holder.

The lamp is lighted, the wick being adjusted to give a small flame for about 15 minutes, and the door of the cabinet being left open to permit the flame to stabilize itself. The zero mark on the scale is adjusted to coincide with the burner top. The cabinet door is then closed and the flame turned up slowly to a height where a smoke spot is formed on the bottom of the dish. The dish is then moved away from the chimney and the flame turned down one-half of one scale division.

This procedure is continued until the maximum height of the flame is produced without a smoke spot forming on the dish. The final adjustment of the flame is made with an accuracy of one-half of one scale division, or 0.05 inch. This maximum height of the flame is read directly by means of the aluminum scale, and represents the quality of the oil with regard to smoke tendency.

A very highly refined kerosene will give a flame height of 3.00 inches or more, a well refined stock about 2.00 inches, and an inferior grade less than 1.00 inch.

Reproducibility

With care and proper attention to details, results on duplicate samples of inferior and well-refined kerosenes should agree within 0.05 inch in flame height; with very highly refined kerosenes within 0.10 inch.

This degree of accuracy will be obtained only if different lamps are as nearly identical in construction as possible. The main variable in a lamp of this kind is the glass chimney, and in the manufacture of this equipment chimneys should be chosen which give identical results. The screen should be kept clean at all times; otherwise the volume of air to the flame will be reduced with corresponding reduction in flame height.

Significance

Increasing the degree of refinement of a kerosene results in an increase in flame height, so that the factor lamp test is a valuable index to the refiner for control of the refining process. In the sulfuric acid treatment of kerosene distillate, the amount of acid used in dumps may at any stage of the treatment be correlated with this lamp test. Furthermore, for kerosene distillate from a known crude source, the amount of acid required to produce a given factor lamp test may be predicted.

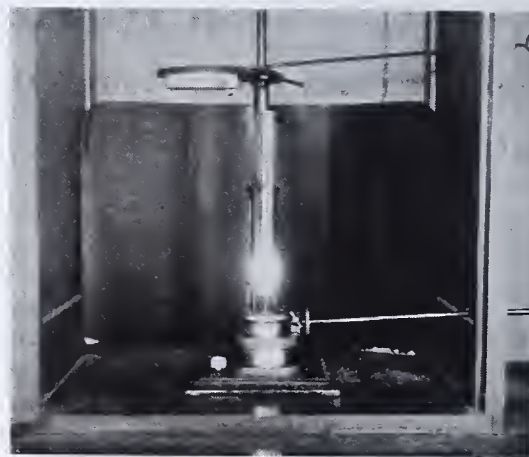


FIGURE 2. IMPROVED FACTOR LAMP

The factor lamp is not designed to give an index of quality for which other lamps, such as the Saybolt standard, the A. R. A. signal semaphore, and Rayo, are more suitable and are now widely used in the industry. Two different kerosenes having the same factor lamp test may be graded differently for quality in another lamp, and vice versa. This will be true for other types of smoke-tendency test lamps. Therefore, when a given grade of kerosene is required to meet a smoke-tendency test, the oil should be tested in a lamp such as the factor lamp, which is designed for this specific purpose.

Summary

A method for the determination of the smoke tendency of refined kerosene is described, by means of which this specific property is evaluated. The actual smoke point is detected with great accuracy, using an ice-cold dish, the flame height at this point being measured directly on the scale. The time required for a test is about 20 minutes, the results being reproducible within 0.05-inch flame height, and for very highly refined stocks within 0.10-inch flame height.

Acknowledgment

Acknowledgment is hereby made of the work done by M. H. Lipp and P. D. Cookson of the Standard Oil Company

Laboratories, Richmond, Calif., in developing improvements in this method which has been used very effectively by this company for several years as a routine test.

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Extending the Useful Range of Concentric Cylinder Viscometers

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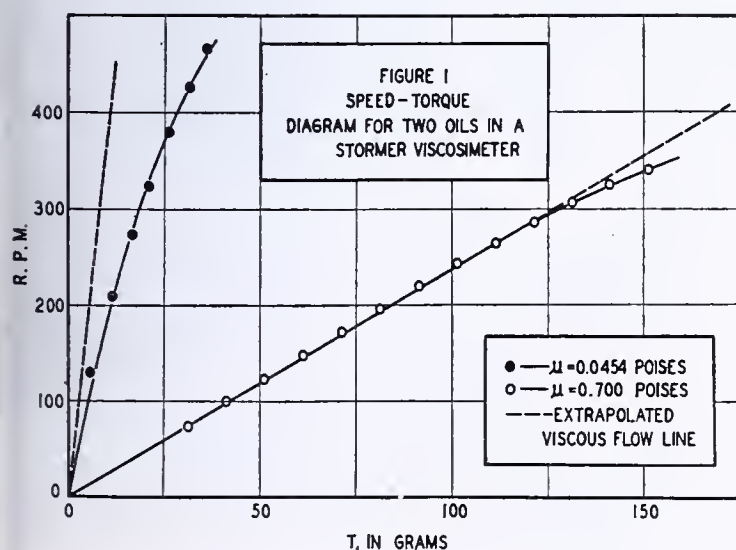
THE convenience of the concentric cylinder type of viscometer for technical work is well recognized. Such instruments as the Stormer, Couette, or MacMichael viscometer combine ease and rapidity of manipulation with considerable flexibility and are accurate enough for many types of industrial problems. However, the application of all these instruments, particularly the Stormer, is limited to liquids whose viscosities are above 0.5 to 1.0 poise—i. e., to liquids from 50 to 100 times the viscosity of water. In consequence, one is forced to use other methods for a great many liquids and solutions of moderate viscosities.

This serious limitation is a consequence of the method employed in calculating the viscosity from the data. If the motion of the liquid is viscous, it can be easily shown that

$$\mu = kT/R \quad (1)$$

where T is the torque acting on one of the cylinders, R is the angular velocity of the rotating cylinder, and k is a constant of the instrument. If the cylinders are concentric, uniform, and sufficiently long for end effects to be neglected,

$$k = \frac{d_2^2 - d_1^2}{\pi L d_1^2 d_2^2} \quad (2)$$



By means of a friction factor-Reynolds number plot it has been found possible to determine the viscosity of liquids in a concentric cylinder viscometer even when the liquids are so fluid that their motion is turbulent during the determination. While the method becomes more inaccurate as turbulence increases, satisfactory results can be obtained with instruments such as the Stormer or MacMichael viscometer for liquids as fluid as water.

where d_1 and d_2 are the diameters of the inner and outer cylinder, respectively, and L is the length of the cylinder over which the viscous drag is being measured.

At large values of R , the motion of the liquid changes from viscous stream-line flow to turbulent flow, and in this latter region T is no longer proportional to R . It is, therefore, no longer justifiable to calculate the viscosity by Equation 1.

Furthermore, the value of R at

which the motion of the liquid becomes turbulent is directly proportional to the viscosity and for liquids of low viscosity will be small. To keep within the viscous region for these liquids, R must be kept so small that all precision is lost.

As an illustration, consider the data of Figure 1, obtained in a Stormer viscometer, in which the torque is proportional to the actuating weight driving the rotating cylinder. With a heavy mineral oil ($\mu = 0.70$ poise), the majority of the points lie on a straight line through the origin and are therefore on the viscous range. The upper end of the line shows pronounced curvature and indicates that turbulence has been developed. For this oil, then, an actuating weight of less than 100 grams should be used if Equation 1 is to be valid. With a light oil ($\mu = 0.0454$ poise), even with the smallest weight considerable curvature is evident, indicating that the viscosity of this liquid cannot be calculated in the conventional way by the use of Equation 1.

The problem of finding the viscosity of a liquid from measurements in the turbulent region may be solved in the following way: From the hydrodynamics of the situation, it is obvious that R is a unique function of the density and viscosity of the liquid, the dimensions of the instrument, and the value of the torque, T .

Define f , the friction factor, as

$$f = \frac{T}{d_1^2 d_2^2 L \rho R^2} \quad (3)$$

From the analogy with fluid flow in pipes, f is a function of the quantity, R_e , which may be termed the Reynolds number, defined as

$$R_e = \frac{R \rho (d_2^2 - d_1^2)}{\mu} \quad (4)$$

Therefore,

$$f = \phi(R_e) \quad (5)$$

where ϕ represents the functional relationship.

In the viscous region, where Equation 1 applies, Equation 5 reduces to the form

$$f = \pi/R_e \quad (6)$$

Consequently, plotting $\log f$ against $\log R_e$ must result in a straight line with a slope of -1 or 45° .

In the turbulent region, the relationship will not in general be simple. However, for a given liquid in a given instrument, there will be only one value of μ corresponding to any given value of f and R_e , and therefore to any given value of R . Consequently, once the relationship represented by Equation 5 has been determined for the turbulent region, the value of f can be calculated by Equation 3 from the measured values of R and T , and μ be calculated from the corresponding value of R_e by Equation 4.

Experimental

The following data were determined with a Stormer viscometer, No. 1114, equipped with a flanged cup and rotating cylinder.

Seven liquids, whose viscosities varied from 0.70 to 0.0059 poise, were used. Six of these were obtained by mixing suitable quantities of a viscous and a fluid mineral oil. The viscosity of each mixture was determined in a Bingham-type capillary viscometer and the densities were measured in a pycnometer. The temperature of calibration and measurement was held constant at 30°C . The seventh and most fluid liquid employed was methyl iodide ($\mu = 0.0059$ poise at 0°C). This liquid was measured at 0°C . and the viscosity and density at this temperature were taken from the International Critical Tables. For each liquid, the speeds of rotation, R , expressed as revolutions per minute were determined for various actuating weights, T , in grams.

By adding 1.4 grams to the value of the actuating weight, the results obtained were corrected for friction in the instrument, for the length of string unwound by the falling weight, and for the weight of the hook on which the actuating weights were placed. This correction is the difference between the weight of the string and hook and the weight necessary to cause the cup to revolve freely in air. The values of the actuating weight shown in Table I include this correction.

The Stormer instrument is not an absolute viscometer. The outer stationary cup is provided with internal flanges, a thermometer well, and other projections, while the internal,

rotating cylinder is hollow and open at both ends. It is therefore not possible to calculate k by Equation 2, although Equation 1 still holds for the viscous region. However, a new friction factor, f' , may be defined as

$$f' = T/\rho R^2 \quad (7)$$

and similarly a new Reynolds number as

$$R_e' = R\rho/\mu \quad (8)$$

where f' and R_e' are proportional to f and R_e , respectively, the constants of proportionality depending on the design of the instrument. It is obvious that Equation 5 holds for the new quantities and Equation 6 may be rewritten

$$f' = K/R_e' \quad (9)$$

where K will now depend upon the instrument, but will not be a simple function of its dimensions.

From the values of R and T determined experimentally, $T/\rho R^2$ and $R\rho/\mu$ were calculated and plotted logarithmically in Figure 2.

Discussion

Inspection of Figure 2 shows that the upper left-hand portion of the curve is a straight line having a negative slope of 45° as predicted by Equation 9. This represents the region of viscous flow. The points in the lower portion of the curve lie on a line possessing a definite curvature. The transition between the linear, viscous portion and the curved, turbulent portion is smooth and gradual, occurring at a value of $R\rho/\mu$ of about 370.

The character of the transition is different from that observed in passing from viscous to turbulent flow of fluids in pipes. In this latter case, the transition is very abrupt, indeed almost discontinuous in character (1). The transition observed in Figure 2, however, is of the type that might be expected from the work of Taylor (2), who found that for the concentric cylinder type of viscometer laminar flow was replaced at high values of $R\rho/\mu$ by a system of regular vortices, occurring at definite positions in the apparatus. In circular pipes, experiments show that the streamline motion is replaced beyond the critical Reynolds number by a random and chaotic distribution of irregular eddies of an entirely different type. At very high values of $R\rho/\mu$, Taylor found that the regular vortex system breaks down into an irregular turbulence similar to that produced initially in pipes. Thus, the transition from an ordered streamline motion to an utterly

random turbulence is much more abrupt in flow through pipes than between rotating, concentric cylinders.

Figure 2 indicates that the transition between viscous and turbulent flow always occurs at a definite value of $T/\rho R^2$, independent of the character of the liquid involved. For this particular instrument, the value is 0.00165. Hence, knowing the density of a liquid, it is possible to determine whether any given measurement of T and R lies in the viscous or turbulent region.

The data on methyl iodide are of interest in showing the effect of density. It is obvious from Equation 1 that in

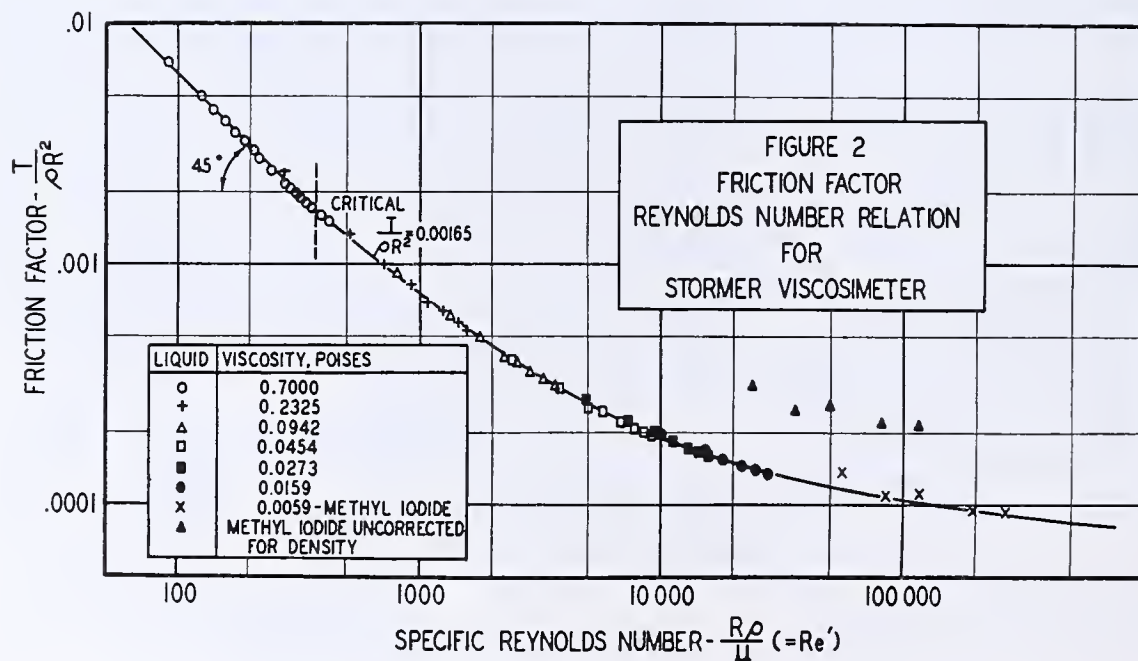


TABLE I. EXPERIMENTAL DATA

(All measurements made at 30° C. except liquid 7)

Liquid	μ , Poise	Density ρ , G./cc.	T Grams	R R. p. m.	$f' = \frac{T}{\rho R^2}$	$Re' = \frac{R\rho}{\mu}$
1	0.7000	0.878	31.4	73	0.00678	91.6
			41.4	98	0.00494	123.0
			46.4	110	0.00439	138.0
			51.4	123	0.00390	154.5
			56.4	136	0.00351	170.7
			61.4	148	0.00321	185.8
			66.4	161	0.00294	202.1
			71.4	173	0.00273	217.2
			81.4	196	0.00244	246.0
			91.4	220	0.00216	276.0
			96.4	232	0.00205	291.1
			101.4	245	0.00194	307.5
			106.4	254	0.00188	318.8
			111.4	265	0.00181	332.3
			116.4	276	0.00174	346.4
			121.4	286	0.00170	359.0
2	0.2325	0.866	131.4	307	0.0016	385.0
			141.4	325	0.00154	408
			151.4	339	0.0015	425
			11.4	74	0.00245	276
			21.4	138	0.00132	514
			31.4	192	0.00099	715
			41.4	243	0.000815	905
			51.4	293	0.000695	1,090
3	0.0942	0.850	61.4	335	0.000636	1,247
			71.4	380	0.000574	1,415
			81.4	420	0.000537	1,564
			5.9	87	0.000918	785
			11.4	148	0.000623	1,338
			16.4	197	0.000504	1,780
			21.4	245	0.000426	2,213
			26.4	280	0.000401	2,530
4	0.0454	0.833	31.4	322	0.00036	2,910
			36.4	357	0.000339	3,223
			41.4	397	0.000312	3,585
			5.9	131	0.000414	2,405
			11.4	208	0.000322	3,820
			16.4	273	0.000257	5,010
			21.4	324	0.000247	5,950
			26.4	380	0.000222	6,970
5	0.0273	0.818	31.4	425	0.000210	7,800
			36.4	465	0.000203	8,530
			41.4	508	0.000195	9,310
			5.9	163	0.000273	4,885
			11.4	252	0.000224	7,550
			16.4	318	0.000201	9,530
			21.4	377	0.000186	11,300
			26.4	435	0.000173	13,040
6	0.0159	0.8034	31.4	480	0.000168	14,400
			36.4	524	0.000164	15,700
			5.9	191	0.000202	9,650
			11.4	294	0.000168	14,850
			16.4	364	0.000157	18,380
			21.4	431	0.000146	21,750
			26.4	488	0.00014	24,610
			31.4	540	0.000135	27,270
7 Methyl iodide	0.0059	2.3303	6.4	142.5	0.00014	54,300
			11.4	214	0.000107	84,500
			21.4	294	0.00011	1,110,000
			51.4	484	0.0000975	1,840,000
			101.4	681	0.0000971	2,600,000

TABLE II. 2.5 PER CENT SOLUTION OF RUBBER IN METHYL IODIDE

(Temperature, 5° C. Density of solution, 2.25)

T Grams	R R. p. m.	T/R	$f' = \frac{T}{2.25R^2}$	$Re' = \frac{R\rho}{\mu}$ (from Fig- ure 2)	$\mu = \frac{2.25R}{Re'}$
21.4	153	0.14	0.00038	2550	0.135
31.4	207	0.147	0.000312	3600	0.129
41.4	254	0.163	0.000276	4500	0.127
51.4	295	0.174	0.000255	5200	0.128
61.4	332	0.185	0.000242	5800	0.129
71.4	368	0.194	0.000229	6500	0.127
81.4	405	0.201	0.000217	7300	0.125
91.4	438	0.208	0.000209	8000	0.124
					Av. 0.128

the viscous region density has no effect on the relation between T and R . This is no longer true in the turbulent region. If the density is neglected in calculating f' and Re' , the resulting values indicated on Figure 2 by the solid triangles are obtained. These points clearly do not lie on the same curve as the other liquids. On correcting for the density, the resulting values form a smooth continuation of the line through the points for the more viscous oils.

As an example of the use of Figure 2, consider the data of Table II for a 2.5 per cent solution of rubber in methyl iodide.

The first two columns give the experimentally determined values of T and R . The progressive increase in the ratio of T/R shown in the third column might lead one to assume an increase in viscosity with rate of shear, but the explanation is of course that the liquid is in turbulent motion. This is shown by the fact that the smallest value of $T/\rho R^2$ is 0.00038, well below the critical value of 0.0016. The fourth column gives the calculated value of f' , and the fifth column, the value of Re' , read from Figure 2. The last column is the viscosity calculated by Equation 5. The average is 0.128 poise with a maximum deviation of less than 6 per cent.

The last column of Table II might be interpreted as showing a small progressive decrease in viscosity with increasing rate of shear or angular viscosity. This behavior, termed anomalous viscosity, is often shown by rubber solutions. However, the small percentage change in viscosity over the considerable range of R makes this somewhat unlikely. The variation shown probably indicates the accuracy of the method. Furthermore, had the viscosity been calculated from the data in the usual way, an increase in viscosity with rate of shear would have been observed (column three of Table II).

It is apparent from an inspection of Figure 2 that the variation of f' becomes progressively smaller as Re' increases to large values. The curve indicates that at sufficiently high values of Re , f' will become constant and therefore the relation between T and R will be independent of the viscosity. It follows, therefore, that the determination of the viscosity from measurements made in the turbulent region has less and less precision as Re increases. However, the data presented here indicate that the method gives results reliable to within 5 per cent for ordinary liquids having viscosities approximating that of water.

Figure 2 is to be looked upon as a generalized calibration curve for the particular instrument employed on this investigation. By the use of a relatively small number of liquids of known viscosities and densities it is a simple matter to construct a similar diagram for any concentric cylinder viscometer, using the method outlined above. Once the diagram has been constructed, one determination of T and R is sufficient to determine the viscosity, irrespective of whether the liquid is in viscous or turbulent motion. It is therefore feasible to make all measurements under one condition—i. e., at a constant value of the actuating weight in the case of the Stormer or a constant r. p. m. for the MacMichael, with a corresponding gain in convenience and ease of operation.

Nomenclature

- T = torque or actuating weight on Stormer viscometer
 R = angular velocity or revolutions per minute of rotating cylinder of Stormer viscometer
 k, K = constants
 d_1 = diameter of inner cylinder
 d_2 = diameter of outer cylinder
 L = length of cylinder over which viscous drag is being measured
 μ = viscosity, poises
 ρ = density, grams per cc.
 f = friction factor = $\frac{T}{d_1^2 d_2^2 L \rho R^2}$
 Re = Reynolds number = $\frac{R \rho (d_2^2 - d_1^2)}{\mu}$
 ϕ = functional relationship
 $f' = T/\rho R^2$ = specific friction factor
 $Re' = R \rho / \mu$ = specific Reynolds number

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Estimation of Milk Solids in Bread

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THE increased commercial use, in bread, of high percentages of milk solids, both whole and skimmed, has stimulated interest in the quantitative determination of milk in bread. This work was undertaken several years ago to develop a reasonably rapid and practical method for this determination.

Until recently little has been published on this subject. Munsey (3) has described the estimation of milk solids by a determination of the fat number, but this method does not give accurate results when skimmed milk only or partially skimmed milk is present. The Hartmann and Hillig (2) citric acid method has also been reported. As citric acid is present in small quantities in milk, the analytical error doubtless is magnified considerably when milk solids are calculated from the citric acid present. The method to be described is based on the determination of lactose and the estimation of butterfat using the Reichert-Meissl number, and applies to skim-milk solids as well as whole-milk solids. It has been in practical use for several years and has given results which are accurate for all practical purposes.

Procedure

Remove the crust of the bread, air-dry the crumb, then grind sufficiently to pass a 20-mesh sieve. Digest 50 grams of the prepared material in 400 cc. of distilled water at about 40° C. for 3 hours, and transfer the mixture to a large centrifuge tube. Centrifuge and decant the liquid portion into a 1-liter volumetric flask. Wash the residue four times, using 75 cc. of distilled water each time, and separate solids by centrifuging. Decant after each washing and add the liquid portion to the first extract. Add 35 grams of Baker's compressed yeast (suspended in a small amount of water), 0.5 gram of ammonium sulfate, and 0.2 gram of sodium bisulfite, and let stand overnight at room temperature stoppered, but with a vent for the escape of carbon dioxide. The ammonium sulfate is used as a yeast stimulant, and the sodium bisulfite retards bacterial action.

After standing overnight add 20 cc. of copper sulfate solution (regular Fehling's A) and sufficient sodium hydroxide solution to give a definite blue color and clarify the solution. Make up to volume in the liter flask, shake, and filter through a good quality filter paper. Take 50 cc. of the filtrate and determine lactose, using the standard Munson and Walker gravimetric method.

Fifty cubic centimeters of the filtrate are equivalent to 2.590 grams of bread after the correction for the yeast is made. The fat-free milk solids are calculated from the percentage of lactose found, and average 50 per cent lactose with only slight variations. Therefore twice the percentage of lactose found (after calculation to the dry basis) is equal to the percentage of fat-free solids on the dry basis of the bread. The accuracy of the method as determined against known formulas indicates that the amount of lactose attacked by the yeast is negligible, and that interfering sugars are completely removed by the yeast.

In order to test the accuracy of the method, breads were baked with varying quantities of fat-free milk and analyses obtained thereon as given in Table I.

The total fat present in the bread is determined by the standard method of the Association of Official Agricultural Chemists (1).

Extract the fat necessary for the Reichert-Meissl number determination by placing 200 to 300 grams of finely ground air-dried bread, depending upon the fat content, in a 2-liter flask containing 1000 cc. of distilled water and 30 cc. of hydrochloric acid. Digest the mass by boiling for 1 hour or until it shows good

digestion, and add 10 grams of Filter-Cel. Filter through a Büchner funnel containing a filter paper upon which is a thin pad of Filter-Cel. Apply suction until the mass is fairly dried. Transfer the residue to a beaker, stir with ether, and filter again through Filter-Cel into a dry flask. Evaporate the ether, and if the oil is clear it is ready for the Reichert-Meissl number determination. About 5 grams of fat are used for this determination, as is usual in the standard Reichert-Meissl method.

The average oil content of flour on the dry basis is 0.7 per cent. This oil has a Reichert-Meissl number of 1, for which allowance must be made in estimating the amount of butterfat in the bread. If other shortening is present, an allowance must also be made for the Reichert-Meissl number of this fat. The normal variation to be expected in the Reichert-Meissl number of butterfat must be considered also.

TABLE I. DETERMINATION OF FAT-FREE MILK SOLIDS IN BREADS

(Moisture-free basis)			
Fat-Free Milk Solids Calculated from formula	Fat-Free Milk Solids Found by analysis	Fat-Free Milk Solids Calculated from formula	Fat-Free Milk Solids Found by analysis
%	%	%	%
0.50	0.52	3.88	4.04
2.40	2.58	4.40	4.56
2.86	3.06	6.00	5.95
3.62	3.56		

The amount of butterfat that would be present if the bread contained whole-milk solids is calculated from the percentage of fat-free milk solids found. The Reichert-Meissl number, after correction for fats other than butterfat present, determines whether the amount of butterfat calculated is actually present. If the Reichert-Meissl number does not indicate any butterfat, skim-milk solids were used in the manufacture of the bread. If the Reichert-Meissl number indicated only part of the butterfat necessary to balance the skim-milk solids in the ratio of skim-milk solids to butterfat in whole-milk solids, then partially skimmed milk was used. The factor 0.4115 multiplied by the percentage of skim-milk or fat-free solids gives the amount of butterfat necessary to balance the skim-milk solids. The Reichert-Meissl number alone without a determination of lactose makes an estimation of the milk solids present quite uncertain.

TABLE II. ANALYSES OF COMMERCIAL WHOLE-MILK BREADS^a

	(Moisture-free basis)				
	No. 1	No. 2	No. 3	No. 4	No. 5
Fat-free milk solids, %	5.76	6.22	6.86	7.56	5.56
Total fat, %	3.98	6.82	6.44	8.56	4.84
Estimated butterfat (fat-free milk solids × 0.4115), %	2.37	2.56	2.82	2.70	2.29
Reichert-Meissl number	13.0	11.5	14.6	10.2	14.5
Butterfat estimated from Reichert-Meissl number, %	1.80	2.60	3.20	2.90	2.40
Whole-milk solids, % (fat-free milk solids plus butterfat estimated from fat-free milk solids)	8.13	8.78	9.68	10.26	7.85

^a For these calculations the Reichert-Meissl number of butterfat was taken as 28.

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Liquid Butane as Motor Fuel

Corrosion Test Methods

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USE of liquid butane as motor fuel involves certain problems in refinement and handling not encountered with heavier fuels. Origin of the particular problems pertinent to this discussion centers in the specialized equipment required for proper vaporization and carburetion of the liquefied gas. Conventional equipment for this service comprises a pressure-regulating valve, a heater, and a butane-metering valve. Presence of minute traces of contaminants in the fuel eventually results in improper functioning of this equipment. In many cases the concentration of interfering material may be so low as to defy detection by ordinary methods of analysis.

Contaminants may be grouped conveniently as insoluble scale and dirt; butane-soluble, noncorrosive, nonvolatile material; and material which is corrosive to metal equipment under service conditions. Insoluble scale and dirt present no great problem since they are normally removed by a metal screen placed in the liquid fuel line ahead of the pressure-regulating valve. On the other hand dissolved nonvolatile material, such as pipe-threading compounds and valve lubricants, even though not corrosive, has a tendency to collect at points of low gas velocity in the metering valve, eventually contributing to improper seating. Particularly objectionable is the corrosive type of contaminant, since it not only destroys the equipment but interferes with satisfactory operation before complete failure occurs.

Any test procedure for determining quality of a given fuel should be rapid and simple, and give results which can be interpreted in terms of actual service. It is believed that such a procedure has been devised for the specific problem outlined.

Method

In principle the method involves inspection of minute quantities of metals which have been exposed to large quantities of the test fuel under conditions representative of, or more severe than, normal service. To facilitate rough visual comparisons and to provide a large contact surface, the metals are prepared in the form of thin copper or silver mirrors on glass. Use of both types of mirror is usually desirable, the former being representative of the metal in the conventional butane heater and the latter having the advantage of pronounced change in appearance in presence of even the slightest trace of corrosive sulfur. Copper mirrors are prepared by reduction of cupric ammonium hydroxide solution with phenylhydrazine (2). Silver mirrors are prepared by the conventional Brashear formula (1), using sugar as the reducing agent.

A sketch of apparatus suitable for contacting the mirrors with the fuel in question is shown in Figure 1. Essential units comprise a steam-heated vaporizer, a 25-cm. (10-inch) section of 1.9-cm. (0.75-inch) gage glass encased in a slotted metal holder, and an orifice gas meter. All parts coming into contact with either liquid or vaporized fuel must be corrosion-proof. Chrome-nickel steel is suitable for metal parts. Any gasket material used in making up tight connections should be of such composition that contamination of the fuel is impossible. Asbestos is a satisfactory packing for sealing the gage glass in its metal holder.

In operation the metal test mirrors, supported, for example, on glass pearls, are packed into the gage glass, and the gage-glass

holder is connected to the vaporizer and the orifice meter. A weighed 75-liter (20-gallon) cylinder of the test fuel is inverted to permit withdrawal of liquid and connection is made to the vaporizer. Steam is turned on and superheated fuel containing the suspected contaminant is passed over the test mirrors. Rate of fuel charge varies from about 5 to 25 kg. (10 to 50 pounds) per hour. Total quantity charge may be as low as 0.5 or 1 kg. (1 or 2 pounds), but with most fuels it is desirable to charge 10 kg. (20 pounds) or more. Exact rate and total quantity are governed by the appearance of the mirrors, care being taken to limit any darkening or other evidence of corrosion to metal in the first 7.5- to 10-cm. (3- or 4-inch) section of the gage glass. For making these adjustments, a control valve is provided in the line between the gage glass and orifice meter. Temperature in the line immediately following the gage glass is maintained at 120° C. (250° F.), control being the steam pressure applied to the vaporizer. After a suitable quantity of fuel has been charged, the feed valve is closed and the cylinder is disconnected and again weighed. The gage glass is then removed from its holder for close inspection of the test mirrors.

Discussion

Many fuels are perfectly clean; so when the test is completed the mirrors are bright, showing no evidence of oil, scum, or color change. The nonvolatile, noncorrosive, butane-soluble type of contaminant is readily detected by the appearance of an oil or scum on the mirror surfaces. When the corrosive type of contaminant is present a rapid change in color is noted—for example, darkening is noted in a few minutes with fuel containing 0.000001 per cent of elementary sulfur.

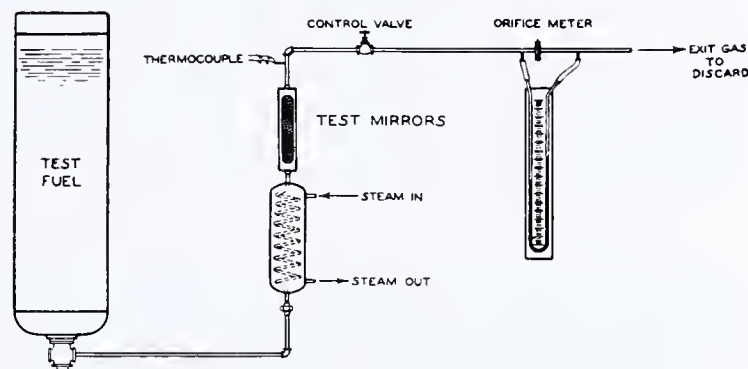


FIGURE 1

Fuel may usually be rated as satisfactory or unsatisfactory on the basis of mere visual inspection of the test mirrors. In cases where qualitative identification of the contaminant is required, the microanalytical procedure to be followed will naturally depend upon the appearance of the mirrors and any clues provided by previous history of the sample. For example, presence of valve lubricant in some fuel samples has been proved by determining saponification number and wax content of the oily scum. Likewise, with another fuel suspected of sulfur contamination, the suspicion was proved correct by decomposition of the darkened copper mirror with zinc and hydrochloric acid and detection of hydrogen sulfide in the gas evolved.

With certain fuels it may be desirable to supplement qualitative identification of the contaminant with critical determination of the quantity present. Such determination is feasible by conventional methods only when the proportion is relatively large—for example, 0.0001 per cent by weight or greater. However, a semi-quantitative index of the concen-

tration of the corrosive type of contaminant may be obtained from an estimate of the surface corroded and the known thickness of the mirror. Thickness of mirrors usually varies from about 3×10^{-5} to 20×10^{-5} mm. (1). Obviously no general rule can be laid down as to the depth of film which an unknown corroding agent will penetrate. In the above-mentioned experiment where sulfur contamination was proved, the copper mirror was about 20×10^{-5} mm. thick and average penetration of the corroding agent was to a depth of only 5×10^{-5} mm. It is suggested, therefore, that mirrors of minimum thickness be employed in tests where more than qualitative information is desirable. By use of thin mirrors it is possible to make a semi-quantitative estimate of the concentration of corrosive type of contaminant when the order of magnitude is only 10^{-7} per cent by weight.

Experience with the test procedure outlined indicates that thoroughly satisfactory results with a liquefied gaseous motor fuel will be obtained only if extreme care is taken to avoid contamination in manufacture, transportation, and transfer to customer's equipment. The following warning instructions are suggested:

1. All fuel tank openings, as well as vapor and liquid transfer hoses, should be capped when not in actual use.
2. When coupling hoses, care should be exercised to prevent entrance of any dust—it may be corrosive.
3. Rubber lining in transfer hoses should be avoided because of possible sulfur leaching. Flexible all-metal hoses or DuPrene-lined hoses are preferred.
4. Valve lubricants should not be used. Although certain types are hydrocarbon-insoluble in the usual sense of the term, the solubilities are sufficient to cause trouble in the present service.
5. Welded pipe connections are preferred. In cases where threaded connections are unavoidable, joint dopes should be used sparingly with attention given to prevent them from entering the fuel system.

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RECEIVED May 13, 1936. Presented before the Divisions of Gas and Fuel Chemistry, Industrial and Engineering Chemistry, and Petroleum Chemistry, Symposium on Motor Fuels, at the 91st Meeting of the American Chemical Society, Kansas City, Mo., April 13 to 17, 1936.

Modification of the Suspended-Level Viscometer

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IN 1933 Ubbelohde (4) published his researches on the development of the suspended-level viscometer, and in 1935 FitzSimons (1) described certain changes and accessories which made the instrument more suitable to the particular requirements of the petroleum industry for accurate and speedy viscosity measurements. While this stage of development has been found to be satisfactory, independent study of constructional and operating details by the authors' laboratory has brought out further modifications in the suspended-level viscometer which have been found advantageous in routine viscosity determinations, as well as research work. It is the purpose of this paper to discuss these features.

Modified Suspended-Level Viscometer

The viscometer shown in Figure 1 consists of two pipet-like bulbs, *A*, connected to two capillaries, *B*, of different radii and sealed to U-tube oil reservoir *C*. Tubes *D* and *E* serve as air vents for producing the suspended level. Leading into the U-tube oil reservoir, *C*, is the helical tube, *F*, through which the viscometer can be filled from the bottom. The entire viscometer is sealed into vapor bath *G* which is heated by vapors from a pure liquid compound boiling in bulb *H*. The vapors surround the entire viscometer, maintaining a uniform temperature throughout. Vapors escaping from the vapor bath are condensed in condenser *I* and returned to bulb *H* through the line, *J*. The liquid in bulb *H* is heated by any convenient means but preferably by an electric heater, *K*. The temperature of the bath is determined by means of a thermometer (not shown) placed in the vapor space, and the temperature can be regulated and maintained constant at any desired point by either the application of pressure or vacuum.

The capillary and air vent tube are connected by means of rubber tubing to a rigid metal manifold, *L*, which has been found to be advantageous when filling, operating, and cleaning the viscometer.

OPERATION. All stopcocks on the manifold, *L*, are closed except 1 and 2. Gentle suction is applied at 1, and the clear oil to be tested is sucked in at the bottom connection, 6, until the U-tube reservoir, *C*, is about two-thirds full. The bottom connection, 6, is closed, suction is withdrawn from 1, leaving this cock open to the air, and the oil is allowed to come to the temperature of the bath. Tube *E* is provided with a second thermometer for determining when the oil is at proper temperature for test.

Stopcock 2 is closed and the oil drawn into the desired capillary by gentle suction at either 4 or 5. When the oil reaches the small

bulb, *M*, the suction is withdrawn, stopcock 3 is opened to the air to form the suspended level, and the flow of oil timed between the two marks x_1 and x_2 of large bulb *A*. As many check determinations as desired can be made by repeating the above procedure, without removing the oil from the viscometer.

The viscometer is cleaned by draining the oil out through stopcock 6. The entire viscometer is washed out with any suitable low-boiling solvent by filling from the bottom, and using the manifold connections as described. Two washes are sufficient and after the final wash has drained, the entire viscometer is dried out by blowing warm, dry filtered air through all cocks and portions of the viscometer proper.

Calibration of Suspended-Level Viscometers

IN TERMS OF KINEMATIC VISCOSITY. The literature (4) and (1) describe the method of calculating a correlation equation for kinematic viscosity in terms of efflux time, based upon accurately measured dimensions of the instrument. However, the authors' preferred method of calibration is against three or preferably more oils of known and representative kinematic viscosity at convenient temperatures, the results of which may be correlated in an equation of the form

$$\text{kinematic viscosity} = At - B/t \quad (1)$$

where *t* equals efflux time in the suspended-level instrument, and *A* and *B* are instrumental constants established by collecting sufficient data to cover the desired range of viscosity. Herschel (2) has used a Higgins (3) plot of the variables

$$\frac{\text{kinematic}}{\text{efflux time}} \text{ versus } \frac{1}{(\text{efflux time})^2}$$

to arrive at these constants for the various technical efflux viscometers, and a like procedure may be used here. Alternatively, since it is usually desirable to have the calibration equation fit the low viscosity calibration data most closely, a procedure somewhat resembling the method of least squares may be applied; however, departing from the conventional method in the use of normal equations in the form

$$\frac{\text{kinematic}}{\text{efflux time}} = A + \frac{B}{(\text{efflux time})^2} \quad (2)$$

$$\text{kinematic} = A (\text{efflux time}) + \frac{B}{\text{efflux time}} \tag{3}$$

It is, of course, characteristic for the algebraic sign of *B* to solve as negative. This method of correlation has the advantage over the usual least squares method in that not only do the deviations in terms of kinematic viscosity balance, but also the fractional (or percentage) deviations.

IN TERMS OF SAYBOLT UNIVERSAL VISCOSITY. While the above method of correlating permits calculation and tabula-

tion of kinematic viscosity in terms of efflux times with a given instrument, it is customary in American petroleum laboratories to refer to Saybolt Universal viscosity at the same temperature. Reference must therefore be had to two equations or tabulations, to transpose from suspended-level time to kinematic viscosities, and thence to Saybolt Universal viscosity.

However, it is a convenient preliminary step, with calibration oils of known kinematic viscosities, to calculate the corresponding Saybolt Universal seconds equivalent, and correlate the latter variable directly (although empirically) with suspended-level viscometer seconds on the same oils, using a procedure resembling the method of least squares, according to the normal equations:

$$\frac{\text{Saybolt}}{t} = A + \frac{B}{t} + \frac{C}{t^2} \tag{4}$$

$$\text{Saybolt} = At + B + \frac{C}{t} \tag{5}$$

$$(\text{Saybolt}) (t) = At^2 + Bt + C \tag{6}$$

A single table can then be prepared which eliminates the step of reference through the intermediate variable of kinematic viscosity. The instrumental constants *A*, *B*, and *C*



FIGURE 2. DETAILS OF VISCOMETER

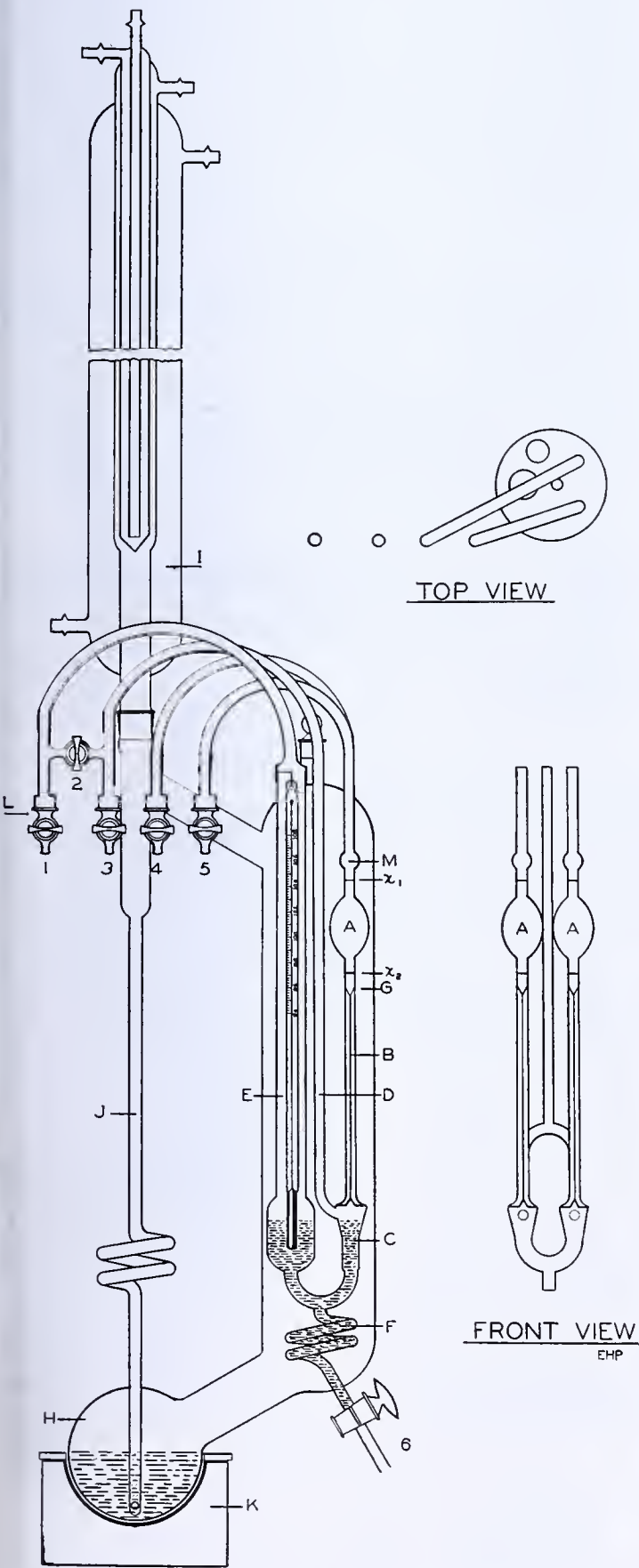
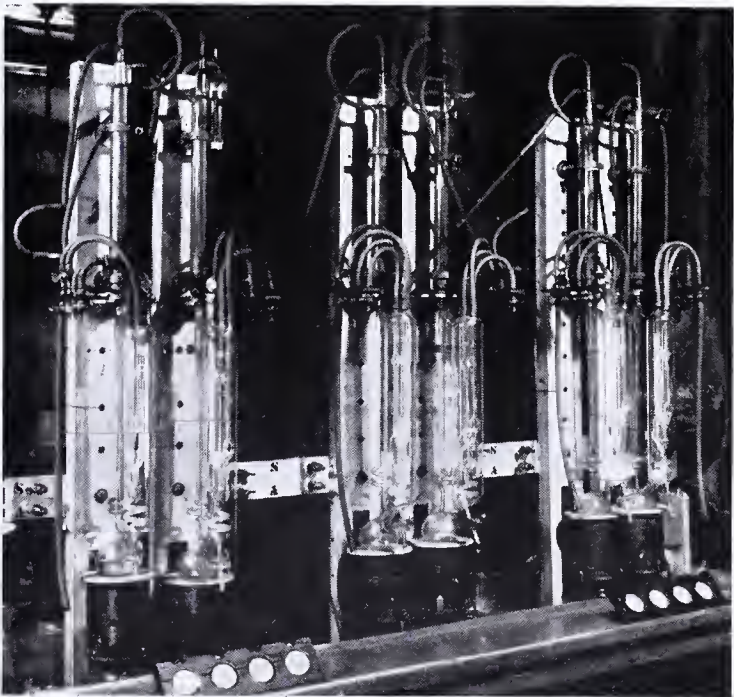


FIGURE 1. DIAGRAM OF VISCOMETER



BATTERY OF VISCOMETERS

are, of course, different from those of Equations 1 to 3, inclusive.

EFFECT OF THERMAL EXPANSION ON CALIBRATION EQUATION. It can be shown by dimensional analysis that in the case of a Pyrex glass capillary viscometer calibrated at 37.78° C. (100° F.) on known oils, and then used for routine measurements at 98.89° C. (210° F.), the calibration equation should theoretically be modified to

$$\text{kinematic viscosity} = 1.0002 A_{100} t - \frac{1.0004 B_{100}}{t}$$

However, within proper limits of design and operation, net error by using a Pyrex viscometer interchangeably at these two temperatures (by using different heating media) is less than one part in 5000, and hence negligible in practical work, as compared to other possible sources of error. In applying a calibration equation over considerably wider temperature ranges, thermal expansion deserves study, as it may become important.

Advantages

The advantages in the use of the modified suspended-level viscometer are:

RIGID METAL MANIFOLD AND THE BOTTOM CONNECTION. From the standpoint of routine viscosity work by nontechnical operators, the importance of permanently connecting all the tubes at the top of the viscometer with rubber hose to a rigid metal manifold, such as that previously described, cannot be overemphasized. It is by means of the rigid metal manifold and the bottom connection that all filling, operating, and cleaning operations are carried out in a viscosity determination. In other words, it amounts to transferring the operations from glass largely to metal, thereby eliminating

the hazards of making hose connections in order to carry out each viscosity determination. Once the manifold is connected it remains so throughout the life of the rubber hose.

The bottom connection, in addition to affording a convenient means of filling and cleaning in conjunction with the manifold, serves as a means of easy and quick adjustment of the oil in the U-tube oil reservoir in case too much oil has been added.

THERMOMETER IN OIL RESERVOIR. The use of a second thermometer in the oil reservoir to indicate when oil is at the desired temperature for test has been found advantageous as to both speed and accuracy in a viscosity determination.

Further, the use of a second thermometer serves to guard against a source of error not generally recognized—an increase in oil temperature above that of the vapor bath caused by the absorption of strong rays of light from solar or electric illumination. A rise of from 0.1° to 0.3° F. has been observed, depending upon the intensity of the light and the color of the oil.

Disadvantages

Unfortunately the suspended-level viscometer is not particularly suited for black oils, because of difficulty in observing the meniscus.

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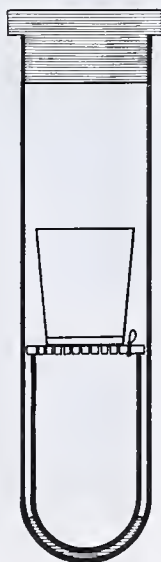
A Centrifugal Filtration Tube

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CENTRIFUGAL filtration is recognized as a rapid and efficient method of freeing crystals from adhering liquid, but the use of a basket centrifuge for this purpose is often impracticable with small amounts of material. Centrifugal filtration tubes for handling such small amounts have been described by Skau (1, 2). In these, the filtering disk rests on a circular constriction in the centrifuge tube; two of the three modifications discussed also have ground-glass joints.

In the accompanying illustration is shown a simple centrifugal filtration tube designed by the writers. Although it can be used for fewer purposes than those described by Skau, it is sturdy, free from ground-glass joints and constrictions, and is readily adaptable to any tube centrifuge. The ordinary tube of the centrifuge is fitted with a filtering crucible, a perforated support, and a container for receiving the filtrate. The tube is closed by a rubber stopper, square-shouldered to prevent wedging. The heavy glass receiving container fits loosely into the



tube, and is cushioned on a rubber pad. The top of this container is ground to support evenly the perforated disk, which also is ground to remove irregularities. A small wire loop is attached to the disk near the edge, so it can be readily removed. The filtering crucible may be a porous-bottomed crucible, a Gooch crucible with or without a filter paper, or a tube with a fritted-glass bottom.

Filtration is made at any desired temperature by bringing the apparatus to that temperature, quickly transferring the wet crystals to the crucible, and centrifuging for about 5 minutes. An estimation of the amount of crystals obtained is readily had by transferring the filtering crucible and its contents to a weighing bottle and weighing. The crystals are then removed and a second weighing is made. This gives the weight of the material by difference, and no error is introduced by any liquid which may be retained by the porous bottom of the crucible.

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RECEIVED May 1, 1936. Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

Estimation of Cuprous Oxide, Cupric Oxide, and Copper in Mixtures

A Microscopical Method

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IN CERTAIN industrial processes, mixtures of the oxides of copper and copper metal occur as by-products, and have commercial value based upon their cuprous oxide content. Macroanalytical methods have been unsatisfactory for arriving at even proximate analyses of these mixtures, but a statistical microscopic method has been found to give a fair estimate of their composition. A method of counting was employed similar to that discussed by Chamot and Mason (1), which involves counting the number of similarly sized particles of each component, thus rendering measurements of volume, weight, and reference substance unnecessary. The method has been successfully applied to textiles, paper, and certain powdered minerals.

In employing a statistical method, it is necessary to develop some simple method of distinguishing between the components in a mixture, in order to facilitate the counting. Characteristics of the components in question are listed in Table I (2, 3).

TABLE I. CHARACTERISTICS OF COMPONENTS

	Mineral	Color	System	D_4^{20}	n_D	Action of Dilute Hydrochloric acid
cuprous oxide	Cuprite	Bright red	Isometric	6.0	2.534	White coating of cuprous chloride
cupric oxide	Tenorite	Iridescent black	Triclinic	6.4	3.18	Dissolves slowly to a green solution
copper	Metallic red	Isometric	8.89	...	Dissolves very slowly

Two methods of distinguishing between components were examined—an optical method and a chemical method. The distinction between components by the optical method was based on the comparative action of reflected polarized light upon isometric cuprous oxide and triclinic cupric oxide. Samples of the two components, cupric and cuprous oxides ground to 100-mesh, were pressed into melted Bakelite with a hydraulic press 75 kg. per sq. cm. (1000 pounds per square inch). Using the customary mineralogical technic, the preparations were polished and examined with reflected polarized light. The tendency of the particles to agglomerate rendered this useless as a statistical method.

The distinction between the components by the chemical method was based on the relative action of dilute hydrochloric acid (15 per cent) on the three components, cuprous oxide, cupric oxide, and copper. Copper metal is unaffected by the dilute hydrochloric acid. Cuprous oxide immediately takes on a white coating of cuprous chloride when the acid is applied. Cupric oxide is unaffected upon immediate application of acid but dissolves slowly on standing. This phenomenon renders the counting simple. The three components exhibit the following colors: copper, bright metallic red; cuprous oxide, creamy white; cupric oxide, iridescent black. They are best observed with reflected light, using a white background for the cupric oxide and a black one for the cuprous oxide.

Experimental

A counting cell was made from a brass washer, 8 mm. in diameter of opening and 2 mm. deep, which was sealed to a microscopic slide with water glass. Continuous use of acid in this

cell is not advisable, but it is satisfactory for at least twenty estimations.

Ten milligrams of the sample (100-mesh) are placed in the cell, six drops of 15 per cent hydrochloric acid are added, and the mixture is stirred with a fine glass rod to distribute the particles uniformly. The cell should be about level full; if not, a drop more of hydrochloric acid is added. The preparation is examined at 100 \times magnification. The direct number of particles are counted in each field, a number of fields being counted. A standard size particle is chosen and other sized particles are rated accordingly. The percentage composition is computed directly from the data. This disregard of volume relationships is made possible by the proximity of the densities of the various components.

This method was applied first to cuprous oxide-cupric oxide mixtures; the results obtained were satisfactory for mixtures containing less than 50 per cent of cuprous oxide. The cupric oxide is more friable and tends to be more finely divided, which makes counting more difficult. The method was also applied to three-component mixtures: cuprous oxide-cupric oxide-copper. The counting was done quickly to avoid solution of the cupric oxide which takes place if the mixture is allowed to stand too long.

TABLE II. RESULTS OF METHOD

Samples	Copper		Cupric Oxide		Cuprous Oxide	
	Present	Found	Present	Found	Present	Found
Known Mixtures						
A ₁	30	39	53	42.5	17	18.5
A ₂	40	39	40	42.5	20	18.5
A ₃	56	54	24	29.0	20	17
A ₄	63	60	6	10	31	30
Unknown Mixtures						
1	12.6	11	63.7	60.7	24.4	27.4
2	0	0	0	0	Pure	100 %
3	0	0	Pure	100 %	0	0
4	14	15.2	36	38	50	46.8
5	9	10.0	38	40	53	50
6	12	14.0	70.0	67.0	18.0	18.3
7	16	16.0	42.5	42.0	41.5	42.0

Summary

A statistical microscopic method for the estimation of the composition of mixtures of cupric oxide, cuprous oxide, and copper is presented, based upon a count of the various particles identified by their chemical properties.

Estimation can be made within 5 per cent of the count value. This is more accurate than the macroanalytical methods.

The time factor is reduced to a minimum.

Acknowledgment

The authors acknowledge the assistance of A. W. Waldo of the Department of Mineralogy in preparation of the specimens for petrographic examination. The unknown samples were prepared by A. Clark.

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RECEIVED May 8, 1936.

The Pendulum as a Source of Energy for Plasticity Measurements

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ADVANCEMENT in methods for studying the consistency of rubber during the last 10 years has been confined largely to various modifications of previous tests and to better interpretation of the data obtained.

The extrusion plastometer introduced by Marzetti (11) has been modified by Behre (1) to provide a battery of instruments, by Dillon and Johnston (5) to provide more simple apparatus capable of operating at increased rates of shear, and by Dillon (4) to provide an instrument for rapid control work. The parallel-plate plastometer (16) has received numerous modifications of form. DeVries (2) modified the plates to provide a constant area of contact with the rubber. This modification was used by van Rossem and van der Meyden (14) who stressed the necessity for following the elastic recovery as well as the rate of compression. Karrer (8) pointed out the need for controlling the time factor during compression and recovery and has described an instrument (9) with which each measurement requires about 30 seconds. The balance plastometer, which employs parallel plates, was described by Hoekstra (7) and is well adapted to following the elastic recovery after the rubber has been compressed under any conditions of thickness and time. A parallel-plate instrument with interchangeable parts to provide various methods of applying pressure and following recovery was described by Lefeaditis (10). The relation between compression and the extent of recovery has been considered by Dillon (3), who concluded that the measurement of either the compression or the elastic recovery as obtained with the usual parallel-plate plastometer was sufficient if the comparison was confined to a number of batches of a given stock or type of rubber. He also pointed out that elastic recovery depends on the speed of the previous deformation. Hoekstra (6), after considering some of the factors involved in plastic flow, concluded that elastic recovery

A pendulum of known potential energy is used to produce a definite, rapid deformation in a plastic material. The damping effect produced on the pendulum is a measure of the energy expended to produce the deformation. The elastic recovery following the rapid deformation is much greater than that obtained with the ordinary parallel-plate instrument. The actual measurement of the energy consumed and elastic recovery requires less than 1 minute. Samples should be brought to a uniform temperature by preheating for at least 10 minutes at the temperature of the test.

should be measured only after compression of the rubber to a fixed thickness. The general usefulness of the parallel-plate plastometer has been greatly increased by the mathematical treatment of Peek (13) and Scott (15).

A third type of plastometer, consisting of a disk which rotates in compressed rubber while the resistance to shear is measured, has been described by Mooney (12).

General Considerations

Manufacturing difficulties are more often due to the elasticity of rubber than to its resistance to flow. Materials

such as lead are easily extruded or rolled into a form which is retained. On the other hand, rubber, after being deformed, never retains its shape perfectly and careful control is required to prevent excessive and sometimes irregular deformation.

The volume flow per unit volume of a material is unlimited. If the flow takes place in an orderly manner, such as that resulting from compression between parallel plates, the total displacement and shear can be determined. If the flow takes the form of internal rearrangement without change of external shape, the shear and displacement usually cannot be determined. An example of the latter type of flow is the mixing of a rubber cement by a paddle immersed in the cement. Both types of flow are unlimited in extent and produce either thorough mixing or very great changes in shape.

On the other hand, the amount of elastic strain in rubber is definitely limited and is a direct result of shearing resistance. The frictional resistance between either elastic particles or plastic and elastic particles in relative motion causes the elastic particles to be strained. The strain increases for any rate of shear until the resulting stress is equal to the frictional resistance, after which no further strain can be produced. The elastic strain will then reach a maximum after sufficient shear has taken place, the exact amount being a function of the elastic properties and resistance to flow of the rubber.

Since recovery depends on the residual elastic strain at the time flow ceases, it follows that elastic recovery will also be some function of the resistance to flow of the rubber. The consistency of rubber would then seem to be determined equally well by measuring either the resistance to flow or the recovery. This may be approximately true if only one grade of rubber is considered. When different types of compounded or uncompounded rubber or other types of material are considered, the relationship between resistance to flow and elastic strain does not remain constant. For this reason, it is necessary to determine both resistance to flow and elastic recovery in each case. The measurement of elastic recovery should be made only after shear sufficient to produce an equilibrium stress. In order to produce a reliable index to the working quality of the material, the deformation should produce a rate of shear comparable to that existing in service.

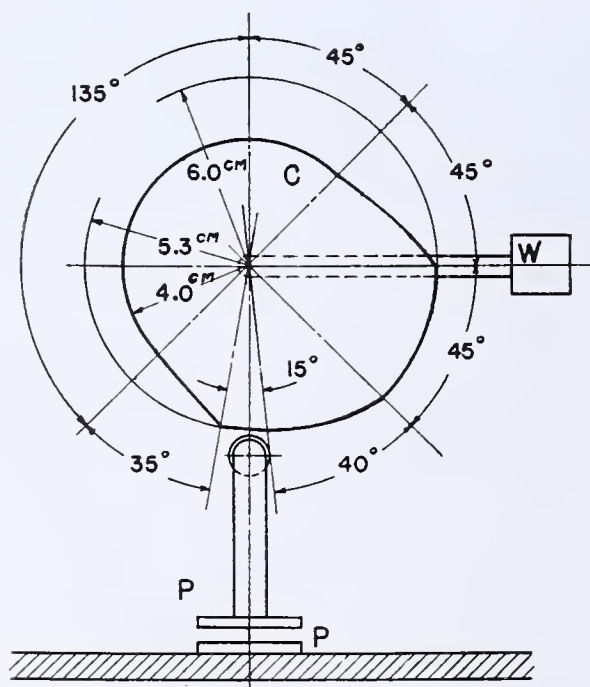


FIGURE 1. DIAGRAM OF APPARATUS

Description of Apparatus

The energy required to produce a definite deformation can be supplied by a pendulum which will also control the time within limits. The quantity of energy required can then be determined from the damping effect produced on the pendulum. The general form of such an instrument is shown in Figure 1. A pendulum, *W*, of known potential energy is brought to rest in a horizontal position. When released, it actuates a cam, *C*, which serves to compress the rubber between parallel plates, *P*. After the pendulum reaches the lowest point the cam rapidly releases the upper plate in order that the elastic recovery may be followed. The pendulum continues its swing and is maintained in position at its maximum height. The amount of energy consumed in the cycle is proportional to the cosine of the angle which the pendulum described in its upward swing.

The instrument which has been designed is shown in Figure 2. The pendulum consists of two weights of 2630 grams each, the center of gravity being on a radius of 7.3 cm. Each weight is attached to a balance wheel of 3710 grams, the combined moment of inertia of which gives the system a period of 0.6 second for a complete vibration. The shaft connecting the two balance wheels carries the cam which actuates the upper plate, a ratchet or maintains the position at any point on the upswing, and a cam which works against a dash-pot and lowers the system to the correct starting position. The driving cam can be replaced by others of different shape for special work. The weight of the upper plate assembly, under which the recovery must take place, is 300 grams. To compensate for the mechanical inefficiency of the system, the pendulum is dropped from 2° above the horizontal position and a complete cosine scale is inscribed on the face of one balance wheel to cover the upswing from the low point to 45° below the horizontal. The wheels rotate with the top moving toward the rear.

Operation is as follows: The instrument is enclosed in an oven which maintains the desired temperature. A forward position of the weights permits the upper plate to be raised sufficiently for inserting the test sample, which is 1 cc. in volume, approximately 10 mm. long, and should be approximately cylindrical. The sample should be preheated for at least 10 minutes before being tested. The weights are then raised to the highest position from which they lower slowly under control of a cam and dash-pot to the starting position. During the descent of the weights to the horizontal, the sample is compressed to a thickness of 7 mm. The weights are then released. During the next 45° rotation the sample is compressed to a thickness of 1.25 mm., at which thickness it is held for an additional 45° before being released. The cosine of the angle of upswing is read and the recovered thickness is recorded after equilibrium is reached, which often requires less than 15 seconds. Highly elastic materials show a slow elastic creep toward the end of their recovery which amounts to a few per cent of the total. In this case the recovery is usually read after an arbitrary time.

The energy consumed should vary with duplicate samples by not more than ± 1 per cent and the recovery should fall within ± 5 per cent of the actual recovered height.

The enclosure of the test sample between sheets of paper can be the cause of nonuniform results. The sample after compression adheres tightly to the paper and must deform the paper in order to recover any portion of its former shape.

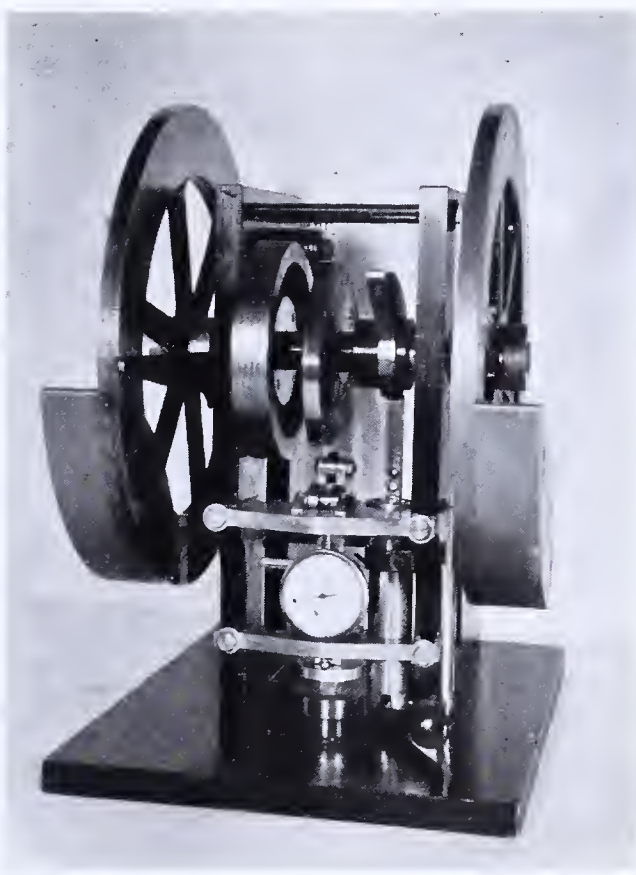


FIGURE 2. PHOTOGRAPH OF INSTRUMENT

Heavy paper requires a large amount of energy for the deformation and produces irregularly projecting wrinkles. Thin, porous paper stretches and slips against the plates during compression by an amount which varies with the resistance of the rubber and disturbs the type of flow produced. If paper is used, the type must be standardized, and unmarked cigaret paper should probably be preferred. Clean test pieces, without paper, talc, or other lubricant, unless excessively tacky, cause no difficulty. Materials such as asphalt and wax which adhere to metal should be run against removable thin metal plates, since the resistance to flow of these materials at high rates of shear is sufficient to tear paper.

The amount of compression adopted was shown by experiment to produce sufficient flow to provide a maximum elastic recovery for most samples of rubber. Very soft rubber tested at 70° C. gave a maximum recovery if compressed

from any thickness greater than 2.5 mm., while tough rubber required compression from a height of at least 6 mm. down to the final thickness of 1.25 mm.

TABLE I. CHANGE IN CONSISTENCY OF RUBBER WITH MILLING

Min- utes Milled	Pendulum Plastometer, 70° C.			Parallel-Plate Plastometer, 70° C.		
	Available energy con- sumed %	Thickness re- cov- ered ^a Mm.	Re- covery %	Thickness after 5 minutes Mm.	Recovered thickness ^a after 1 minute Mm.	Re- covery %
5	55.6	6.85	548	5.35	7.12	33.1
	53.8	6.40	512			
	54.5	6.82	546			
10	51.0	5.15	410	4.27	5.47	28.2
	50.2	4.95	396			
	52.0	4.98	399			
	48.6	4.57	366			
15	50.0	4.34	347	3.95	4.96	25.6
	49.0	4.65	372			
	49.0	4.52	361			
	46.7	2.73	218			
	46.8	3.10	248			
20	48.0	2.96	237	3.71	4.50	21.3
	46.7	1.55	124			
	45.8	1.64	131			
	45.7	1.55	124			
30	46.7	1.49	119	3.30	3.81	15.5
	44.8	0.92	73			
	44.8	0.96	77			
45	44.8	0.92	73	2.82	3.26	17.0
	44.8	0.96	77			

^a Thickness recovered is the increase in thickness from the thickness of greatest compression. Recovered thickness is the total thickness of the sample.

The amount of energy available for compressing the rubber depends on the shape of the cam. The cam described compresses the rubber during only the first 45° rotation of the pendulum, which limits the amount of energy available to the cosine of 45° times the potential energy of the pendulum at the starting position or to a reading of 70.7 on the instrument scale. The substitution of a cam which compresses the rubber through an angle of 90° would make available the total potential energy of the system.

Experimental Part

The type of results obtained with the pendulum plastometer is illustrated by the following experiment. Two thousand

grams of pale crepe rubber were milled on a 45×20 cm. mill, through which water at 50°C . was circulated. The temperature of the rubber was approximately 70°C . during the milling. Samples were removed at intervals for test. The consistency of the rubber was followed by means of both the pendulum plastometer and the parallel-plate plastometer (16). The results are shown in Table I. Several sets of data are shown with the pendulum instrument, in order to illustrate the degree of duplication. The samples run in the pendulum plastometer were in direct contact with the metal plates.

TABLE II. ENERGY CONSUMPTION AND ELASTIC RECOVERY

Material	Available Energy Consumed %	Thickness Re- covered Mm.	Recovery %
Rubber 100, mineral oil 30	24.8	0.53	41.4
Rubber 100, mineral rubber 50	37.5	0.41	32.8
Mineral rubber (0.5-cc. sample)	68.0	0.07	5.6
Tire tread stock	67.0	4.03	322.0
Balata	57.3	0.54	42.1

The data obtained with the two instruments are directly comparable only in regard to the elastic recovery. The pendulum instrument shows not only a much higher recovery, but a much greater difference between the extremes. The thickness index of the parallel-plate plastometer, while not indicating a quantitative energy relationship, has a greater percentage spread than the energy consumed by the pendulum instrument. The thickness index is probably satisfactory for following the uniformity of a given material. The energy consumed should, however, be a more reliable index for a comparison of various rubber compounds or other materials.

While a more or less definite dependency exists between the elastic recovery and energy consumed by different samples of the same rubber, this relationship varies considerably when

different rubber compounds or other substances are considered. This is illustrated by the data in Table II, which shows the results of tests on various compounds and substances.

The early stages of vulcanization are detected with the pendulum plastometer by the rapid change in the elastic recovery. In many cases the elastic recovery will double before a noticeable difference is found in the energy consumed.

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The Preparation of Naphthidine

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STRAKA and Oesper (8) showed that naphthidine (4,4'-bi-1-naphthylamine) is a satisfactory oxidation-reduction indicator, particularly as an internal indicator in the volumetric determination of iron and chromium by means of dichromate. None of the methods hitherto available (1, 2, 3, 6, 7) for the preparation of naphthidine has been found satisfactory, for they are either laborious or yield only small specimens of this compound. A simple and practicable procedure has now been worked out, and the preparation of naphthidine in adequate quantities is here described. The starting materials are cheap, the time required is reasonable, and the yield of the finished product is good. The procedure may be divided into two stages: (1) the preparation of azonaphthalene, and (2) the reduction of the azonaphthalene to hydrazonaphthalene, which is not isolated but immediately rearranged to naphthidine (Figure 1).

Preparation of Azonaphthalene

The following modification of Lange's (5) method was found most suitable for the preparation of azonaphthalene:

Thirty-five grams of α -naphthylamine hydrochloride are stirred into 500 cc. of water in an 800- to 1000-cc. beaker, 17.5 cc. of concentrated hydrochloric acid are added, the mechanical stir-

rer is started, and the solution is cooled in an ice bath to about 0° . Cold diluted sulfuric acid (21 cc., sp. gr. 1.84, plus 200 cc. of water) is then stirred in. The suspended amine salt is diazotized (by vigorous stirring, with customary precautions as to temperature) by slowly adding a cold solution of 14 grams of sodium nitrite dissolved in 80 to 100 cc. of water. The reddish brown solution of the diazonium salt is allowed to stand 5 minutes (good cooling), and filtered at the pump, the filtrate being received in a precooled filter flask surrounded by an ice bath. The cold filtrate is transferred to a 2-liter beaker (ice bath), the stirrer started, and a cold solution of 66 grams of anhydrous sodium acetate in 300 cc. of water slowly added, the temperature being kept between 0° and 5° . A cooled solution of 31 grams of sodium sulfite in 200 cc. of water is then run in slowly, a vigorous evolution of nitrogen ensues, and 1,1'-azonaphthalene begins to separate. After the addition of the sulfite solution has been completed, the stirring is continued for 5 minutes. The suspension is then taken out of the ice bath, and warmed on a water bath, and the tan or orange precipitate is filtered off, washed, and dried on a porous plate.

The average yield of crude azonaphthalene, melting at 180° to 184°C ., is 31 grams (calculated 27.5). Pure azonaphthalene melts at 186° (3), 188° to 189° (4). The product obtained by the present procedure can be used for the preparation of naphthidine without further purification; in fact, the moist filter cake can be carried directly into the next step.

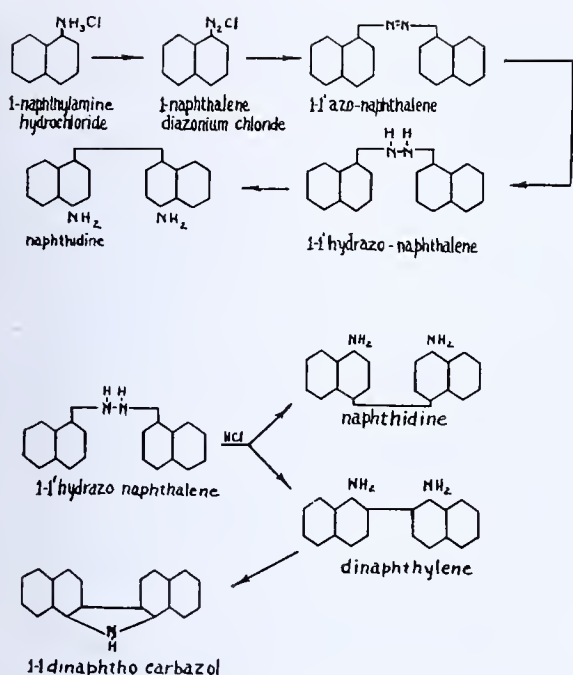


FIGURE 1

Reduction of Azonaphthalene to Hydrazonaphthalene and Rearrangement into Naphthidine

Twenty grams of crude azonaphthalene are suspended in 200 cc. of ethanol, and brought to a weak boil. A solution of 40 grams of stannous chloride in 100 cc. of concentrated hydrochloric acid is slowly run in (with occasional shaking) until the

suspended solid has turned light tan. The heating is immediately discontinued, the suspension is cooled to room temperature, and 100 cc. of concentrated hydrochloric acid are added to precipitate the rest of the naphthidine hydrochloride. Under no condition must the solution be heated with the acid, since the dinaphthylene (1,1'-diamino-2,2'-dinaphthyl) present in the solution, when heated with hydrochloric acid, loses ammonia, forming dinaphthocarbazole, which precipitates with the naphthidine hydrochloride and greatly impedes its purification.

The naphthidine hydrochloride is removed from the cooled suspension, sucked as dry as possible, suspended in 200 cc. of water, and 20 per cent sodium hydroxide solution is added in slight excess. The mixture is kept warm for 10 minutes at about 40° C., stirring frequently. The crude naphthidine is filtered, washed with water until free of alkali, then sucked dry as possible. The crude base is boiled up with 120 cc. of ethanol, and pyridine (40 to 45 cc.) slowly run into the boiling suspension until the solid has dissolved. Any obvious impurities are removed by filtering the hot solution. The filtrate is allowed to cool slowly, and the naphthidine separates in well-formed crystals, sufficiently pure for indicator purposes (m. p. 198–199°). Twenty grams of azonaphthalene produce 6 grams of purified naphthidine, corresponding to 33.5 per cent yield, calculated on the naphthylamine hydrochloride originally taken.

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An Adiabatic Calorimeter

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A sensitive adiabatic calorimeter is described in which the rate of oxygen absorption and the rate of temperature change due to the heat of reaction of finely divided substances with oxygen are measured. A differential thermopile and a photoelectric relay maintain adiabatic conditions; an electronic relay and an electrolysis cell make possible the automatic control of oxygen pressure. For certain samples of bituminous coal at one atmosphere pressure and at 50° C. initial temperature, oxygen absorption and temperature rise are nearly linear functions of time and one may be predicted from the other with considerable accuracy.

IT WAS desired to measure simultaneously the rate of oxygen absorption and the rate of temperature change induced by the heat of reaction of finely divided substances with oxygen at about 50° C. and at atmospheric pressure. To accomplish this purpose, a sensitive adiabatic calorimeter was constructed in which substantially no heat interchange between sample and environment was possible. Included in this apparatus were an automatic compensator to maintain constant oxygen pressure and a nitrometer tube from which

the volume of oxygen was read. Davis and Byrne (1) investigated the oxidation characteristics of various coals with an adiabatic calorimeter. In their apparatus the temperature of the calorimeter liquid was made by electrical means to follow closely the temperature of the coal. Kohman (3) studied the effect of oxygen absorption on the aging of rubber. For maintaining constant oxygen pressure over the sample, his apparatus employed an automatic compensator. Specifically, a manometer was so constructed that any decrease in pressure due to an absorption of oxygen caused a mercury-platinum contact to close and permitted an electric current to flow through a solution of oxalic acid. The gases liberated by electrolysis forced mercury into a nitrometer tube and thus decreased the volumetric capacity of the system and restored the original pressure. The volume of oxygen was then read directly from the nitrometer tube.

The calorimeter described here is a combination, with some modifications, of the above two types of apparatus. To ensure an even temperature, the entire reaction unit, which is a closed system, is immersed in the calorimeter bath. Heat of reaction is measured as a function of the temperature of the bath, and the oxygen absorption is read from the nitrometer tube. The adiabatic control and the control of oxygen pressure are automatic.

Control of Adiabatic Conditions

The adiabatic calorimeter is a modified de Khotinsky aquarium-type thermostat bath of about 300 liters (79 gallons) capacity. Figure 1 shows an assembly sketch of the complete apparatus. A turbine-type stirrer efficiently agitates the water of this bath, and an external spill-over device serves to supply continuously

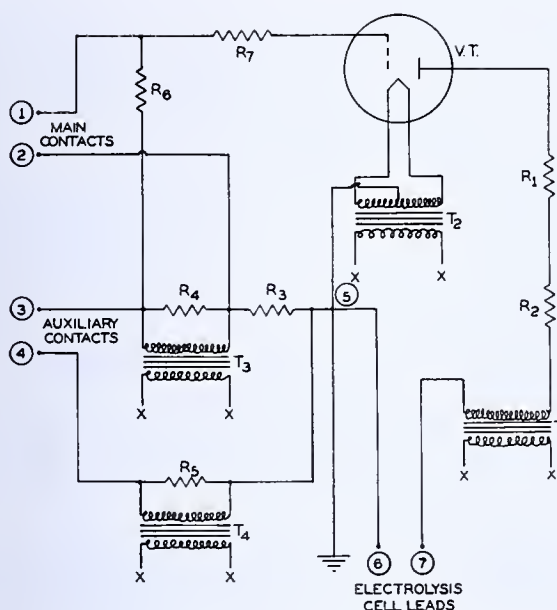


FIGURE 3. WIRING DIAGRAM OF ELECTRONIC RELAY

- | | |
|-----------------|--|
| R_1, R_2 | 50-watt 110-volt lamps |
| R_3, R_4, R_5 | 500-ohm resistors |
| R_6, R_7 | 100,000-ohm resistors |
| T_1 | 1 to 1 ratio insulating transformer |
| T_2 | 2.5-volt 10-ampere filament transformer |
| T_3 | 7.5-volt filament transformer |
| T_4 | 15-volt filament transformer |
| X, X | 110-volt alternating current connections |
| $V. T.$ | Westinghouse Type KU-627 Grid-Glow tube |

produce strains which cause breakage, this number is kept to the minimum required for rigidity of mounting of the glass tubing.

The accurate measure of the oxygen absorption is entirely dependent on the unfailing operation of contacts 1 and 2 and, subsequently, the relay controlling the electrolysis in B_4 . Hence, by the use of an electronic relay, the power handled by these contacts is so small that any danger of fouling is precluded even in an atmosphere of oxygen. The Westinghouse Type KU-627 Grid-Glow tube requires a minute amount of power in its grid circuit to control a relatively large amount of power output in its plate circuit. This tube, therefore, is used as the relay; contacts 1 and 2 control the grid circuit while the electrodes in the electrolysis bulb, B_4 , are connected in series with the plate circuit of the tube. When the tube ionizes or passes current, a pulsating direct current, obtained by rectification of the alternating current output of plate transformer T_1 (Figure 3), passes through B_4 , to produce electrolysis of the concentrated oxalic acid solution in B_4 . Figure 3 shows a circuit that is conventional in many respects, but that embodies certain innovations which are necessary in this work.

Filament current and control grid voltage are supplied by transformers T_2 and T_3 . The circuit for the main contacts, 1 and 2, is entirely conventional—that is, the closing of these contacts reduces the control grid voltage to zero, allowing the tube to pass current, R_6 and R_7 being current-limiting resistors. For the operation of contacts 1 and 2 alone, the current through R_3 (500 ohms) is too small to cause an appreciable voltage drop.

Since it is necessary to block any further electrolysis when mercury has completely filled the nitrometer tube, contacts 3 and 4 are added to the above circuit. T_4 is connected to have the same polarity with respect to the filament as T_3 . The closing of contacts 3 and 4 produces a voltage drop across R_3 which is equal to the difference in voltage between T_4 and T_3 (7.5 volts) and which is negative with respect to the filament when T_1 is positive with respect to the filament. Complete blocking of ionization, therefore, results as long as 3 and 4 are closed. It is apparent that the state of contacts 1 and 2 has no effect on the operation of the tube in this condition because 7.5 volts negative is more than sufficient to prevent the tube from passing current. The current handled by contacts 1 and 2 is estimated at approximately 7.5×10^{-5} ampere. After nearly a year's continuous

operation, no fouling of these contacts has been noted. Contacts 3 and 4 handle a much larger current, but their operation is too infrequent to cause wear.

It is essential that point 5 of the electronic relay be well grounded. The brass frame of the apparatus, the Phototroller, and the electrostatic shield of the phototube cord should all be grounded at this point. However, electrostatic shielding of the leads from the electronic relay is unnecessary; rubber-covered cable is sufficiently insulated when the specified parts of the apparatus are well grounded.

Adjustment and Operation of the Apparatus

Adjustment of the apparatus for adiabatic control is the first step when a run is started. The zero of the galvanometer is adjusted to bring its reflected beam of light to the center of the phototube housing. During this operation, the galvanometer terminals should be shorted. One of the halves of the adjustable shutter is removed from the phototube housing, while the other half is screwed towards the center of the housing until it just intersects the reflected beam of light. With this adjustment, the movement of the beam in one direction has no effect on the phototube, but a movement of approximately 0.7 mm. in the other direction is enough to energize the phototube, and to trip the relay in the Phototroller. Polarities are so arranged that the light strikes the

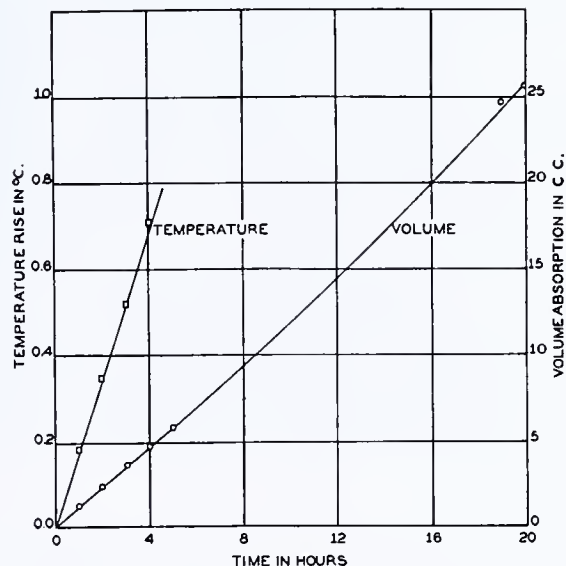


FIGURE 4. CURVES FROM TYPICAL RUN

phototube when the bath drops below the temperature of the sample. When the bath heats slightly above the sample, the e. m. f. of the thermopile actuates the galvanometer to shift the beam of light back onto the shutter and causes the relay to turn off the current to the intermittent heater. The rheostat for the continuous heater is adjusted so that the intermittent heater is on and off for the same period of time. For good operation, one cycle requires about 1 minute; the intermittent heater is on and off for equal periods of 30 seconds. The temperature variation of the bath, during one cycle, is about 0.007°C. as estimated with a Beckman thermometer. By allowing the Phototroller to take control when the bath and sample, in an inert atmosphere, are at the same temperature, the accuracy of this adjustment is easily checked. As a result, no drift in the temperature of the bath should take place over a 24-hour period.

The manipulation of the unit in the thermostat will be illustrated by reference to Figure 2.

First, 75 grams of the finely powdered sample are placed in the Dewar reaction flask. As the case may demand, air above the sample is replaced by oxygen or nitrogen. Evacuation is controlled by S_3 with S_2 and S_4 open; S_1 is open to the atmosphere.

Just before the mercury reaches stopcock S_2 , it is closed, and evacuation is completed in the remainder of the system. Now oxygen is slowly admitted to the system through S_3 until atmospheric pressure is reached, after which S_2 is opened and the pressure in the nitrometer tube is allowed to rise to atmospheric by additional oxygen admitted through S_3 . To assure the removal of all air from the system, this procedure is repeated two additional times.

In the following manner the final adjustment of pressure is made: In the assembly of the apparatus, mercury was added to B_1 until its level in the nitrometer tube was a few millimeters above the first graduation. At this point in the adjustment, a pressure, slightly above atmospheric, is placed on the system by the manipulation of S_3 , thereby depressing the mercury level in the nitrometer tube. Now, S_1 is opened to the electrolysis cell, B_4 , which is at atmospheric pressure, and then S_4 is closed, isolating the gas in B_2 from the system. In this procedure the final step is the adjustment of pressure in the system to bring the level of mercury in U-tube H up to contact 1. This is done by allowing gas to leak from the system, through S_3 , until the pressure in B_2 is sufficiently above that in B_3 to complete the circuit of contacts 1 and 2. The flash of light, caused by the ionization of the Grid-Glow tube in the electronic relay, instantly shows when mercury reaches contact 1. As a result, the pressure in B_2 is about 1 mm. above atmospheric, but the pressure in B_3 and in the reaction flask is approximately atmospheric.

The automatic control of pressure, in the apparatus just described, is based on the pressure of the gas in B_2 when S_4 is closed. When a slight amount of oxygen is used up by the sample, the pressure in B_3 is decreased by a corresponding amount. Consequently, this drop in pressure allows the gas in B_2 to force the mercury in H upwards, until contact 1 is closed. When this happens, the grid in the electronic relay loses control,

and the tube passes current through the electrolysis cell, B_4 . The gases thus formed pass through S_1 into B_1 , causing an increase in pressure and a rise in the mercury level in the nitrometer tube. This decreases the volume of the system until the original pressure, which breaks contact 1 and stops the electrolysis, is restored. To operate the device, only a small fraction of a millimeter difference in pressure between B_2 and B_3 is required.

In a normal run, bulb B_2 serves a further purpose when the temperature of the bath is rising continually. An increase in temperature tends to cause an increase in volume of the gas in the system; but, since the tendency is equal in B_2 and B_3 , and since B_2 is closed from the system, the two tendencies are counter-balanced through U-tube H . The gas in the system is, therefore, of constant specific volume, and consequently, no correction factors are applied to the readings of the nitrometer tube.

Figure 4 shows temperature increase and volume absorption curves, plotted as a function of time, for a typical run. At 50° C. these curves deviate only slightly from straight lines, but do show an upward tendency in 20 hours. For a given sample of bituminous coal, the correlation between temperature increase and oxygen absorption is sufficiently good to predict one accurately from the other.

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Location of the Antienzyme in Egg White

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FOR many years it has been known that raw egg white resists proteolytic digestion. At first it was thought that this resistance was due to the inherent character of the various proteins of the egg white. Sugimoto, according to Needham (3), was the first to show that egg white contained an antienzyme which was responsible for this resistance to proteolytic action.

Balls and Swenson (1), while studying proteolysis in stored eggs, found that this antienzyme was located in the thin white. The thick white was found to contain a sufficient amount of trypsinogen to liquefy it a few hours after activation with enterokinase. In this work Balls and Swenson did not separate the thin white into the inner and outer fractions. Since these two kinds of thin white are formed by entirely different processes (2) and serve different functions, there is no reason to assume that they are alike in antienzymatic action.

Method

In this investigation the method described by Balls and Swenson was followed, with the exception that the thin white was divided into inner and outer portions.

The portion of the egg white to be tested was incubated for 30 minutes with a solution of enterokinase, buffered with an ammonia-ammonium chloride mixture, and a solution of casein was added. The acidity of this mixture was determined immediately by titrating an aliquot portion with 0.1 *N* alkali, using thymolphthalein as an indicator. The remainder of the mixture was incubated 30 minutes, after which the increase in acidity was taken as a measure of the proteolytic activity.

The egg white was divided into three fractions—outer thin, thick, and inner thin—by breaking the egg into a Petri dish. A sample of the outer thin was removed with a pipet, and the remainder of the outer thin was carefully removed with filter

paper. The thick portion was then cut with scissors to allow the inner thin to run out. A sample of this inner thin fraction was pipetted off and the remainder of this fraction was removed with filter paper. The remaining thick white was separated from the yolk and chalazae with a suitable pipet. The thick white was finally forced through a fine-meshed screen to render it soluble in the digestion mixture.

While this procedure is not suitable for quantitative determination of the amount of each fraction, it does give a representative sample of each of the three fractions for analysis. Samples from five eggs were pooled for each determination which was made in the afternoon on eggs laid the same morning. In addition to determining the proteolytic activity of the three fractions separately, determinations were also made on mixtures of equal volumes of inner thin and thick, and outer thin and thick. The results are given in Table I.

TABLE I. PROTEOLYTIC ACTIVITY OF EGG WHITE

(Differences in acidity for the various fractions and mixtures, before and after incubation, as measured in cc. of 0.1 *N* alkali.)

Determination	Outer Thin	Thick	Inner Thin	Thick and Outer Thin	Thick and Inner Thin
1	0.52	0.55	0.16	0.95	0.18
2	0.04	0.10	-0.44	0.06	-0.30
3	-0.04	0.60	0.01	0.64	0.02
4	0.08	0.54	-0.26	0.64	-0.16
5	0.18	0.90	0.01	1.22	0.43
6	0.13	0.50	-0.13	0.52	0.09
7	-0.14	0.24	-0.07	0.06	-0.08
AV.	0.11	0.49	-0.10	0.56	0.02

In each of the seven determinations the thick white showed distinct proteolytic activity, which is in accord with the results of Balls and Swenson. When the inner thin was mixed with the thick in equal proportions, the proteolytic activity

was reduced in each case. In contrast with this, when the outer thin was mixed with the thick, the proteolytic activity of the mixture was greater than that of the thick alone in five cases, practically equal in one, and less in one of the seven determinations. These results indicate that most of the inhibitory substance responsible for the resistance of raw egg white of freshly laid eggs to proteolytic activity is located in the inner thin fraction.

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Preparation of Flattened Copper Tubing Coils

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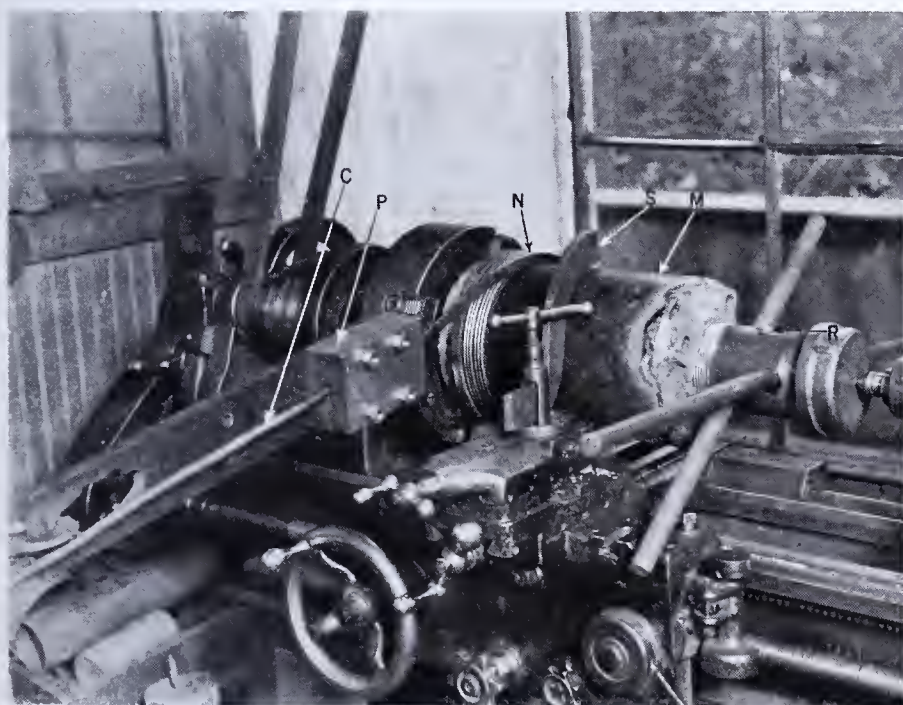


FIGURE 1. FLATTENED COPPER TUBING COIL IN THE MAKING

FLATTENED copper tubing may be used more advantageously than circular tubing in many types of laboratory and experimental apparatus.

FORMING THE FLATTENED TUBING. Flattened copper tubing may be readily formed by drawing circular tubing through special dies. In 1926 William L. Barrett made two dies for forming flattened copper tubing: one for forming tubing 0.5625×0.1875 inch with an opening 0.4375×0.0625 inch from 0.375-inch copper tubing having 0.0625-inch wall; the other for forming tubing 0.75×0.21875 inch with an opening 0.625×0.09375 inch from 0.5625-inch tubing having 0.0625-inch wall.

MAKING COILS OF FLATTENED TUBING. Numerous spirally wound coils of flattened copper tubing have been made in the metallurgical laboratories of the Pittsburgh Station of the United States Bureau of Mines, a mandrel being made for each diameter of coil required. The photograph, Figure 1, shows a coil in the making.

The mandrel, *M*, 7 inches in diameter, is mounted in a lathe. Flattened copper tubing *N* was formed as circular copper tubing *C* was drawn through the die, *P*, and simultaneously wound on the mandrel. The mandrel was hand-rotated by means of bars inserted into the holes, *R*. The curved tool, *S*, held the turns together and prevented the flattened tubing from twisting as it was wound onto the mandrel.

JOINING FLATTENED COPPER TUBING It was often necessary to join pieces of flattened copper tubing. None of the

numerous joints made by this method has failed; they are tight and strong, and do not decrease the cross-sectional area of the flattened tubing. The details of the joint are shown in Figure 2.

A is the jig for forming the sleeve, *B* the parts of the joint, and *C* the completed joint in a section of flattened copper tubing. A piece of copper tubing about 1.25 inches long, having an inside diameter equivalent to the outside diameter of the tubing to be joined, was shaped on the jig, *A*, the cross section of which was the same as that of the flattened tubing to be joined. If a piece of the larger tubing is not available, the short piece may be easily made by turning and drilling a piece of copper rod.

Two methods of completing the joint have been used: (1) The inside of the sleeve and about an inch of the end of each piece of tubing were coated with silver solder. Borax was used as a flux. The silver-solder-coated ends were inserted in the sleeve as shown in *C* and sweated together by heating with a small-tipped oxy-acetylene torch, after which the ends of *b* were silver-soldered to *a* and *c*,

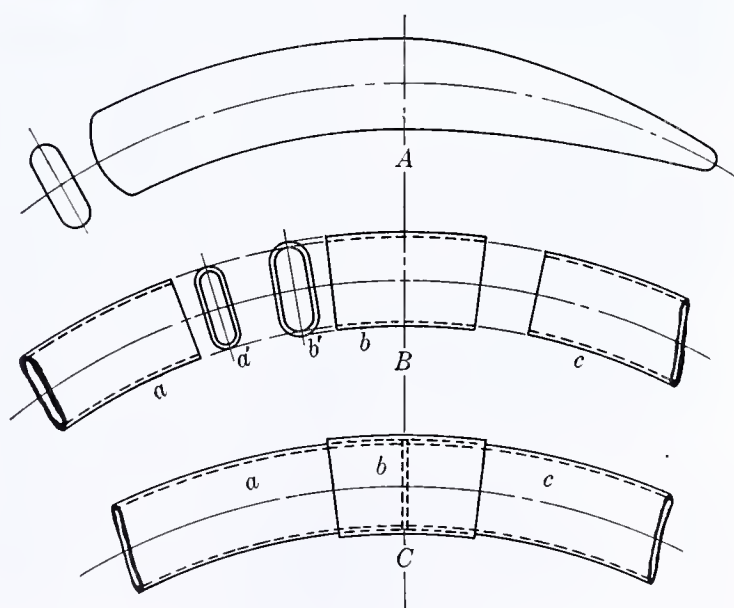


FIGURE 2. METHOD OF JOINING FLATTENED COPPER TUBING

respectively. (2) The ends of the tubing were inserted in the sleeve as shown in *C* and the ends of *b* silver-soldered to *a* and *c*, respectively.

RECEIVED April 27, 1936.

A Precision Melting Point Apparatus

EMANUEL B. HERSHBURG, Converse Memorial Laboratory, Harvard University, Cambridge, Mass.

THE determination of the melting point of organic compounds by the capillary method is at present complicated by an abundance of different types of apparatus, involving errors of varying magnitude and varying widely in sensitivity and ease of manipulation. For purposes of research involving new compounds it is imperative that the data obtained shall be of a higher degree of accuracy than that required for identification and this in turn demands an apparatus itself free from error. When this is accomplished it follows that manipulation will be easier and sensitivity correspondingly greater.

From a consideration of types of apparatus and of heating, medium of heat transfer, and thermometers, which have been discussed at length in the literature (5), it was apparent that a mechanically stirred and electrically heated cyclic liquid bath was best. The Thiele melting point apparatus (8), one of the earliest cyclic designs, has been modified by Avery (1), Markley (4), and Conte (2), to permit mechanical stirring, and electrical heating has been recommended by Pratt (6), Dennis (3), Sando (7), and others. No one apparatus, however, completely fills the demands of research and this explains some of the existing discrepancies in melting points.

In the ideal apparatus there should be a zone adiabatic relative to the external surroundings and it should be possible to immerse the mercury column of the thermometer completely without requiring excessively long capillary tubes. This is closely approached by the apparatus described below, in which at equilibrium the lateral or vertical temperature deviation in the zone enclosed by the sleeve is

within $\pm 0.025^\circ \text{C}$. At the same time a ball-bearing glass stirrer ensures rapid circulation, so that with increasing temperature the rate of rise of this zone is essentially constant. The sleeve further serves to guide both thermometer and melting point tubes and in conjunction with the cap which acts as a support permits insertion of new tubes without removing the thermometer.

Internal electrical heating is by far the most sensitive and most readily controlled, but no organic liquid has been found that will withstand elevated temperatures without rapidly darkening. Sulfuric acid is undesirable in this connection because it is electrolyzed and the gas bubbles obscure

the determination; nevertheless it is perfectly satisfactory when used with external heating.

Apparatus

The melting point apparatus (Figure 1) consists of a Pyrex glass cyclic bath, A, with a glass stirrer, H, running in ball bearings and externally heated by electricity. The portion in which the determination is made carries the soft glass sleeve, D, with sealed-on platinum loops which guide both thermometer and tubes. The sleeve forms an annular space which isolates the cooler wall liquid from that coming in contact with the instrument, and is centered by small knobs, I, near the top and bottom. Caps F and G fit snugly into the tubes, F having two small holes at the base of the thermometer tube for the insertion of the melting point capillaries. It also has a small wedge which fits into a lip, J, in the vertical tube and prevents rotation due to the twisting action of the circulating liquid on the thermometer. Stirrer H is of glass tubing and has a two-bladed propeller driven by a small synchronous motor. It just clears tube A but rotates with ample clearance at the enlargement. It runs in two ball bearings which are slipped on over short lengths of thin-walled rubber tubing well moistened with glycerol. The liquid circulates in a clockwise direction.

The heating element is wound on the curved portion, E, and consists of 300 cm. (10 feet) of No. 28 B. and S. gage wire with a resistance of 0.14 ohm per cm. (4.1 ohms per foot), using about 325 watts at 115 volts. First a layer of 0.078-cm. (0.031-inch) asbestos paper is wound on the glass in segments, preferably while wet, and the surface is rubbed gently to make a perfect coating without cracks. After this first layer has dried an appropriate length of cotton string (240 cm. or 8 feet) is wound on and evenly spaced. The wire is anchored to a brass terminal and wound on parallel to the string, which is then removed. A

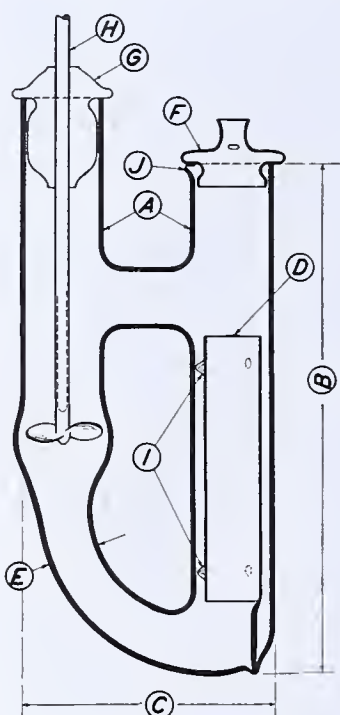


FIGURE 1. DIAGRAM OF APPARATUS

- A. 28-mm. outside diameter and 25-mm. inside diameter
- B. 17 cm.
- C. 8.5 cm.
- D. Sleeve, 19-mm. outside diameter, 17-mm. inside diameter, 9 cm. long. Loops No. 26 B. and S. gage platinum wire
- E. 18-mm. outside diameter
- F. Thermometer cap. Thermometer tube 7-mm. inside diameter
- G. Stirrer cap
- H. Stirrer, 5-mm. outside diameter glass tubing. Ball bearings with 0.61-cm. (0.25-inch) hole and 2.2-cm. (0.875-inch) outside diameter, unground
- I. Knobs to center sleeve.
- J. Lip and wedge to prevent rotation of cap

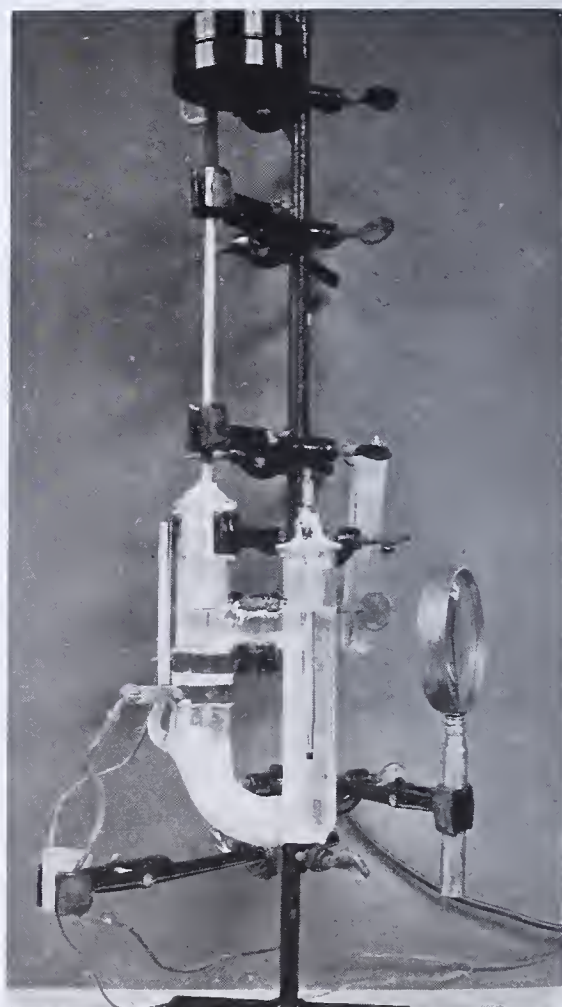


FIGURE 2. PHOTOGRAPH OF APPARATUS

second layer of asbestos is put on in a similar manner and the remaining 60 cm. (2 feet) of wire are wound back with wide spacing so that both leads come out on the same side. Finally a top layer of asbestos is put on. Connections are made to brass clamps shown in Figure 2. The current is controlled by a 200-ohm rheostat of 3-ampere capacity or by an auto-transformer.

Capillary melting point tubes are of conventional size and sufficiently long to extend at least 0.93 cm. (0.375 inch) below the top of the sleeve. They are supported by small steel clips of a type commonly used for display purposes, clamped to short lengths of 0.3-cm. (0.125-inch) thin-wall rubber tubing.

The tube is slipped in one of the holes in the cap and guided through a platinum loop. The thermometer is supported by a narrow rubber band fastened near the top and rests on the central tube of cap *F*.

INTERNAL HEATING. For this purpose 180 cm. (6 feet) of No. 32 B. and S. gage wire with a resistance of 0.33 ohm per cm. (10 ohms per foot) are wound into a spiral, annealed at red heat, and inserted in the curved portion so that one lead comes out the tube at the back (shown in Figure 2, but not in Figure 1) and the other comes out at the lip under cap *F*. In this case about 200 watts are ample for heating the tube and the same controls may be employed as above.

Operation

The apparatus described is suitable for the conventional short Anschütz enclosed-scale thermometers, but the over-all dimensions are not critical and may be varied over considerable limits. Sulfuric acid is added to a point level with the top of the upper horizontal connecting tube and the stirrer operates at a speed just below the point at which cavitation occurs.

Using two identical thermometers and a special sleeve without platinum loops, the temperature difference between points 0.62 cm. (0.25 inch) from the top and bottom of the sleeve was measured at equilibrium conditions and was found to be approximately $\pm 0.025^\circ \text{C}$., or within the limits of accuracy of the thermometer reading. There was no observable lateral deviation from the center of the tube to the sleeve wall. Without the sleeve, however, the vertical deviation was about 0.2° and the lateral deviation from the center of the tube to the wall was considerably greater, depending on the closeness of the outer thermometer to the wall of tube A.

With external heating the bath rose from 40° to 200°C . in 7 minutes and to 280° in 14 minutes. If the tube was externally heated at the maximum rate and the current shut off at 100° , the temperature rose 7° , while at 250° it rose about 1° . With internal heating a much smaller amount of power raised the temperature over the same interval in about 12 minutes and the maximum overshoot was only about 1° or 2° .

The highest temperature reached with concentrated sulfuric acid was about 295°C . and at this point smooth, steady ebullition took place without bumping. With Nujol paraffin oil as the bath fluid and heating internally with a 200-watt element, the temperature rose to about 310°C . Unfortunately the oil darkened rapidly and other organic fluids behaved similarly.

The rheostat was calibrated for the equilibrium temperatures reached after about 0.5 hour at a setting and this greatly facilitates subsequent determinations. The rate of rise may be readily controlled by setting the rheostat at a predetermined number of degrees above the thermometer temperature, while maintaining this difference by continually decreasing the resistance.

Gas heating also gave satisfactory results. In this case the tube was heated at the curved portion, *E*, after first winding on a single layer of No. 22 B. and S. gage copper wire.

Acknowledgment

The author is indebted to L. F. Fieser and M. S. Newman for helpful suggestions and criticisms.

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RECEIVED April 15, 1936.

A New Type of Laboratory Stirrer

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THE stirrers shown in the photograph have proved very satisfactory for stirring mixtures thick with solid where the propeller type of stirrer is ordinarily useless. In such instances as condensation reactions with sodium, the preparation of benzalacetophenone, the Blanc reaction, and some Friedel-Crafts reactions the stirrers shown have performed good service where other types failed. Unlike propellers, these stirrers can be made much larger than the mouth of the flask and the wires swung sufficiently to permit insertion as shown in the upper left-hand example. Once inside, they follow the contours of the flask without scratching and are even more easily removed.



NEW TYPE OF LABORATORY
STIRRER

Various alloy wires of No. 18 B. and S. gage may be used, depending on the type of reaction. In particular, chromium-nickel and copper-silver alloys have been found to be very resistant to attack and have the requisite stiffness and resilience.

Stirrers of all types run more smoothly and for longer periods of time with a minimum of attention if ball bearings are used as guides. In general two sets spaced a few inches apart are necessary and are best fastened by inserting a piece of rubber tubing with the inside well moistened with glycerol and then slipping the whole on the glass tubing as shown in the lower center of the photograph. Ordinary commercial unground ball-bearing assemblies 2.2 cm. (0.875 inch) in outside diameter and having a 0.94-cm. (0.375-inch) hole used in conjunction with 6.5- to 7-mm. glass tubing have proved a very satisfactory and inexpensive combination for general use. An occasional drop of oil is all the lubrication necessary.

RECEIVED April 9, 1936.



A New Moisture Tube

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ALTHOUGH numerous devices utilize the principle of distillation with an immiscible solvent for the measurement of moisture in many classes of materials, the one described here is new and possesses certain advantages. It is designed for use with a water-immiscible solvent, such as carbon tetrachloride, which has a greater density but a lower boiling point than water. It has been used during the last seven years in the Hercules Powder Company laboratories for the routine determination of water in dynamite.

The method of operation of the apparatus, as shown in Figure 1, is obvious. The apparatus is constructed of Pyrex glass. The bottom of the moisture tube fits into a 500-cc. round-bottomed flask, and an Allihn water condenser is fitted into the top. (This moisture tube may be secured from Otto R. Greiner Co., 55 Plane Street, Newark, N. J.) To maintain a constant minimum hang-up of water in the condenser, the tip of the condenser either should be beveled at 45° to 60° or else be constricted and provided with a vapor inlet as indicated. The latter arrangement is preferable. Because the return arm is surrounded by a continual stream of hot vapors, there is no tendency for water to separate and accumulate at any point in the liquid-return system. This important advantage makes possible higher accuracy than usually is obtained by other distillation methods.

This moisture tube has the advantage of being very compact; thus, a supply of moisture tubes can be conveniently kept in sulfuric acid-potassium dichromate solution when they are not in use. This conforms with the requirement that all forms of apparatus in which small volumes of water are measured must be kept scrupulously clean.

Calibration of Moisture Tube

Fill the U-tube with carbon tetrachloride, then add about 0.25 gram of distilled water. Again add carbon tetrachloride dropwise, until a drop falls through the water layer. This produces an upper meniscus of uniformly reproducible curvature. Record the volume between the bottom of the upper meniscus and the top of the lower meniscus; this is a zero reading. Then add 2 to 3 grams of water, weighed to the nearest 0.005 gram, and repeat the readings as described. The weight of water, added as the second portion, will correspond to the increase in volume measured on the graduated scale, if the tube is accurately graduated. Repeat this procedure to check other portions of the scale.

Determination of Apparatus Correction Constant

The amount of water collected in the moisture tube is measured by reading the bottom of the upper meniscus and the top of the lower meniscus. This arbitrarily chosen manner of reading the tube does not include the water actually in the tube which is above the bottom of the upper meniscus and below the top of the lower meniscus. Furthermore, a small

TABLE I. RESULTS OF DETERMINATIONS WITH KNOWN AMOUNTS OF WATER PRESENT

Determination	Water Present Grams	Water Found Grams	Error Gram
1	0.50	0.51	+0.01
2	0.50	0.49	-0.01
3	1.00	0.95	-0.05
4	1.00	0.97	-0.03
5	1.03	0.98	-0.05
6	2.00	2.01	+0.01
7	2.00	1.96	-0.04
8	3.00	2.99	-0.01
9	3.00	3.03	+0.03
10	4.00	3.97	-0.03
11	4.00	4.01	+0.01

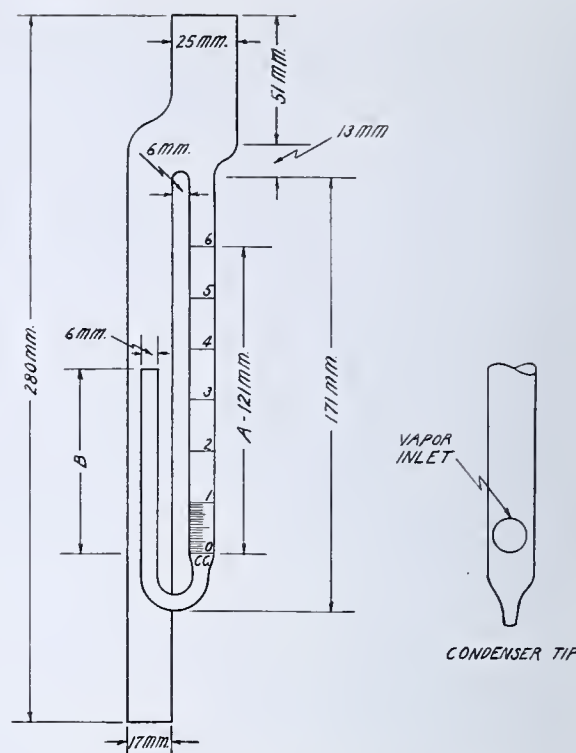


FIGURE 1. HERCULES MOISTURE TUBE

It is important that the ratio of length A to length B be the same as the ratio of density of solvent to density of water. If carbon tetrachloride is used as the solvent, A/B should be 1.6. Dimensions given are approximate. The measuring tube is graduated in 6 or 7 1-cc. divisions, numbered as indicated and marked with 0.05-cc. subdivisions.

amount of water is always present in the carbon tetrachloride at equilibrium and a small amount may adhere to the condenser. Therefore, an additive apparatus correction constant must be applied to compensate for all the water present in the apparatus which is not actually measured. This additive correction constant was established as 0.11 gram, by making 45 determinations with 7 different moisture tubes and known amounts of water. The following procedure was followed for determining this additive correction constant:

Four grams of a dry absorbent material—Kieselguhr, for example—were placed in the distilling flask. Then a known amount of water was added, followed by the regular charge of 200 cc. of carbon tetrachloride. The absorbent material was placed in the flask to absorb the water and to simulate usual working conditions. The distillation was conducted in the usual way until a maximum amount of water had been collected. The amount of water added less the amount of water collected equals the apparatus correction constant, expressed in grams.

Procedure for Determination of Moisture

Weigh a sample of suitable size into a 500-cc. round-bottomed flask. Add 200 cc. of carbon tetrachloride and connect the flask to a moisture tube and 30-cm. (12-inch) Allihn condenser, both of which are clean and dry. Heat the flask at such a temperature that the carbon tetrachloride falls from the tip of the condenser in a steady stream for a period of 3 hours or until the volume of water in the measuring tube reaches a constant maximum value.

By means of a pipet, add carbon tetrachloride dropwise until a drop just falls through the water layer. Immediately read the position of the bottom of the upper meniscus and the top of the lower meniscus. The difference between these two readings, plus a constant correction of 0.11, is the amount of water present expressed in grams.

The results given in Table I were obtained with the moisture tube just described and serve to show the accuracy and precision of the method. It is believed that this method will find useful application in many analyses where the rapid determination of moisture by distillation with a solvent such as carbon tetrachloride is desired.

RECEIVED April 28, 1936.

Organic Combustion Apparatus for Highly Volatile and for Inflammable Liquids

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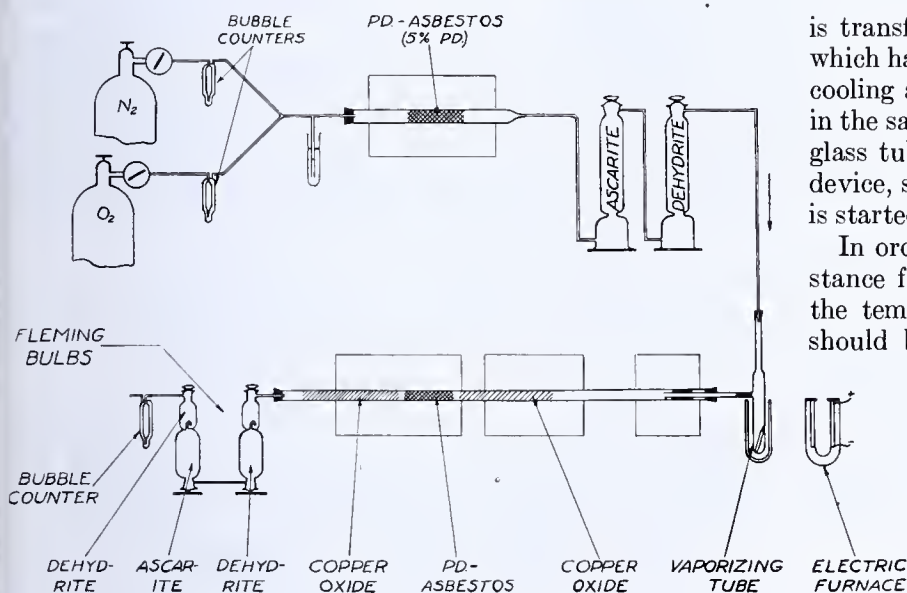


FIGURE 1. ORGANIC COMBUSTION APPARATUS

IN ESTABLISHING the purity of low-boiling hydrocarbons, such as propane, the carbon-hydrogen ratio may be used as a convenient supplement to other criteria such as freezing point, boiling point, molecular weight, etc. For this purpose organic combustion analyses of the greatest possible accuracy are essential, and special precautions are necessary in order to avoid explosions which are likely to occur whenever the concentration of the inflammable vapor in the combustion tube becomes large enough to reach the explosion limit with oxygen or with the oxygen-nitrogen mixture, when used.

In principle the combustion apparatus used is identical to that published by Reid (2) and is shown in Figure 1. As indicated in Figure 2, a controlled evaporation of the sample is accomplished by attaching to the combustion tube a separate vaporizing tube made of quartz. The dead space at the bottom of the vaporizing tube enables the operator to evaporate the sample at a low rate, even in a rapid stream of oxygen. Thus, a gas mixture well below the explosion limit is ensured in the combustion tube and the secondary oxygen or air is obviously eliminated.

The samples to be analyzed are cooled and inclosed in sealed Pyrex glass tubes which have been drawn out into a fine capillary opening at one end. In sealing this open end with the oxygen flame, all hazards are removed if a stream of nitrogen is directed toward the tip of the cooled glass tube while the flame is being applied. Considerable pressure will develop within the glass bulbs in which low-boiling samples are sealed when they are allowed to warm up to room temperature. However, such low-boiling liquids as propane (boiling point $-42.2^{\circ}\text{C}.$) have been kept in this manner in a desiccator for weeks without the occurrence of a single breakage.

When the sample tube is ready it

is transferred carefully into the vaporizing tube (Figure 2) which has been cooled in advance by immersing it in a proper cooling agent. As soon as a sufficient cooling of the liquid in the sample tube has been effected, the capillary tip of the glass tube is broken off by means of any suitable breaking device, such as the one shown in Figure 3, and the combustion is started.

In order to control the evaporation of the low-boiling substance from the vaporizing tube into the combustion tube, the temperature of the cooling mixture in the Dewar flask should be maintained well below the boiling point of the sample. By gradually lowering the Dewar flask, a steady and uniform evaporation of the liquid may be accomplished in about 15 minutes.

In working with liquid mixtures such as lower boiling petroleum fractions, motor fuels, etc., a brownish residue is frequently found in the sample tube when the vaporization of the low-boiling liquid has been completed. In order to complete the combustion of this residue, the Dewar flask is replaced with the electric heater shown in Figure 2, after which the temperature of the lower part of the vaporizing tube is increased to a dull red heat. The electric heater may also be used for controlling the evaporation and the rate of combustion when higher boiling liquids (boiling point above $70^{\circ}\text{C}.$) are being analyzed. Here it is advisable to heat the small copper spiral between the vaporizing tube and the rubber stopper to a dull red heat by surrounding a small section of the tube with an electric heating coil.

Organic combustions of highly inflammable liquids, such as low-boiling petroleum fractions, are preferably carried out in an atmosphere consisting of a mixture of nitrogen and oxygen as indicated in Figure 1. In order to avoid explosions the amount of oxygen in such cases is increased from about 40 per cent by volume at the beginning of the combustion to 100 per cent at the end of the combustion.

The apparatus shown in Figure 1 has been in use for over 3 years, during which time organic combustions have been

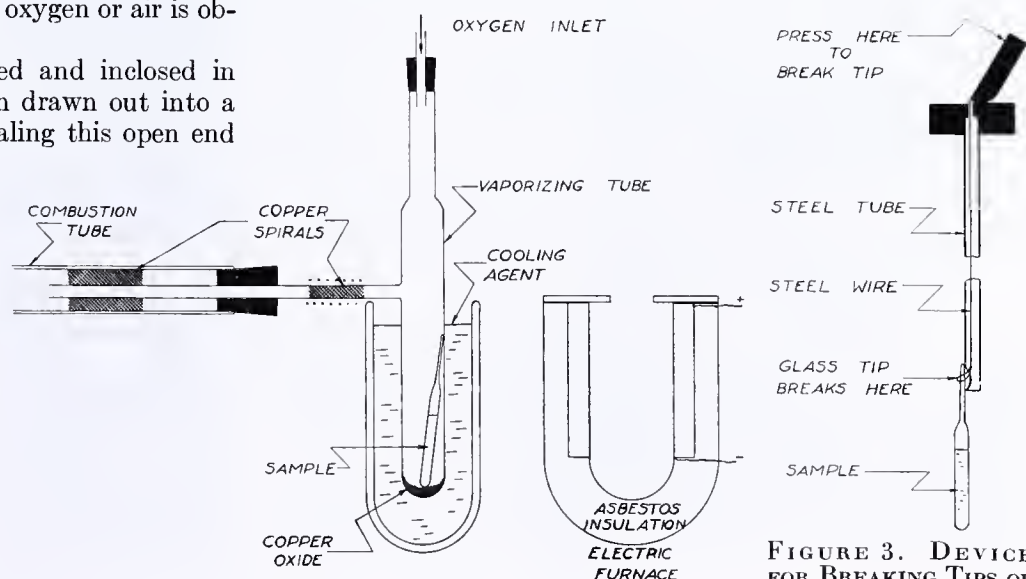


FIGURE 2. VAPORIZING TUBE

FIGURE 3. DEVICE FOR BREAKING TIPS OF SAMPLE TUBES

TABLE I. RESULTS OF THE COMBUSTIONS

Sample	Run	Hydrogen		Carbon		Sum	Carbon-Hydrogen Ratio	
		Found %	Deviation from mean value %	Found %	Deviation from mean value %		Found	Deviation from mean value
Commercial propane fraction (contains propylene)	1	17.64	-0.02	82.22	-0.02	99.86	4.66	+0.01
	2	17.68	+0.02	82.26	+0.02	99.94	4.65	0.00
	3	17.65	-0.01	82.20	-0.04	99.85	4.65	0.00
	Av.	17.66	82.24	99.88
Cracked petroleum fraction (boiling between 25° and 50° C.)	1	14.37	-0.02	84.82	+0.02	99.19	5.90	+0.01
	2	14.41	+0.02	84.78	-0.02	99.19	5.88	-0.01
	Av.	14.39	84.80	99.19	5.89
<i>n</i> -Heptane	1	16.01	-0.05	83.76	-0.08	99.77	5.23	+0.01
	2	16.09	+0.03	83.87	+0.03	99.96	5.21	-0.01
	3	16.09	+0.03	83.89	+0.05	99.98	5.21	-0.01
	Av.	16.06	83.84	99.90	5.22
Theoretical		16.10	83.90	5.21

made of a very great number of low-boiling petroleum fractions without the occurrence of a single explosion.

The data shown in Table I indicate that the results can be duplicated with an accuracy of about 0.05 per cent, even if rubber stoppers are used at both ends of the combustion tube.

For greater accuracy all rubber connections in Figure 1 should be eliminated and replaced with ground glass-to-glass, glass-to-copper, or quartz-to-quartz joints (1).

If a separate combustion tube is used for the analysis of liquids only, it is evident that, since the usual combustion boat has been eliminated, the vaporizing tube and the combustion tube may be made in one piece, thereby eliminating the rubber stopper between them. In such case the section of the combustion tube which is normally used for the boat and for the copper spiral may be either entirely omitted or filled with copper oxide.

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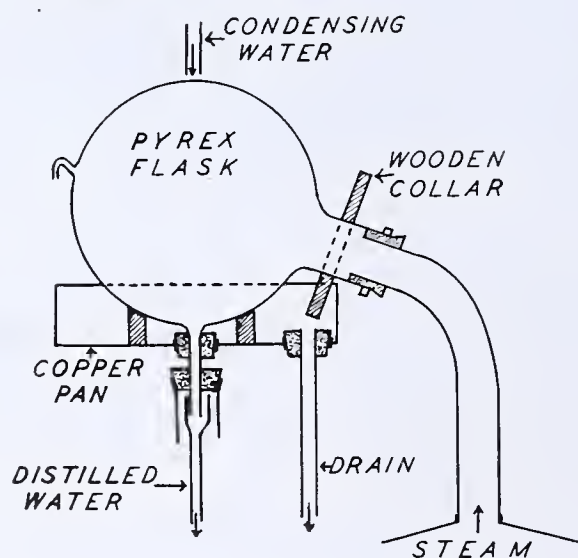
Glass Head for a Laboratory Water Still

PAUL F. SHARP AND EARLE B. STRUBLE

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TWO large Pyrex flasks, joined by a goose neck of wide-bore glass tubing, have been used for large-scale laboratory vacuum distillations in various laboratories for a number of years. In this laboratory two 23-liter flasks are used, one serving as the distilling flask, the other as the condenser, with the cooling water flowing over the outside.

Difficulty with the repeated loosening of the tubes in the head of laboratory water stills, which permitted a trace of the cooling water to enter the stream of distilled water, led to the trial of a Pyrex flask as a stillhead. A 5-liter flask was used on a steam-heated still with a capacity of 8 liters (2 gallons) an hour. The glass stillhead was satisfactory and has been in almost daily use for about 2 years.



The arrangement used is illustrated in sufficient detail to make its construction clear. The curved neck and the return of a small amount of the condensed water reduce entrainment. The transparency of the condenser permits the inspection of its operation. The condensing surface is large. The cooling water cannot enter the distilled water supply. The condenser can be readily cleaned.

RECEIVED February 17, 1936.

A Simple Micro- and Macro-Kjeldahl Steam Distillation Apparatus

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Division of Sugar Plant Investigations, Riverside, Calif.

THE Kjeldahl distillation apparatus shown in Figure 1 possesses all the advantages of the apparatus now on the market and yet is so much simpler in design that it can be built by the average laboratory technician without difficulty and at a comparatively low cost.

By placing a steam chamber, C, between the steam generator, B, and the distilling chamber, F, the steam jacket and its two large ring seals are eliminated, which is the chief difficulty encountered by the ordinary laboratory technician.

The distillation is carried out with all stopcocks closed. The generated steam passes through the steam chamber, C, to the distilling chamber and then through the trap, G, to the cooled condenser. The water formed from the first steam which condenses in the steam chamber keeps the large 4-mm. stopcock cool and out of contact with the passing steam.

With suction applied at I by means of the aspirator, the sample is removed and ammonia-free rinse water drawn up the condenser tube through the trap, G, and down into the distilling chamber, through the steam chamber, C, and into the sink.

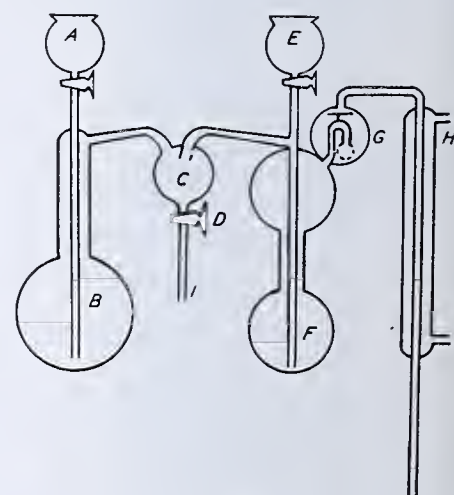


FIGURE 1

RECEIVED January 15, 1936.

INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

Sulfur in Plain and Alloy Steels

A Critical Study of the Combustion Method

C. H. HALE, JR., United States Steel Corporation, Kearny, N. J., AND W. F. MUEHLBERG, American Steel and Wire Company, Cleveland, Ohio

THE methods employed heretofore for determining sulfur in steels have not been entirely satisfactory with respect to speed and accuracy, particularly when applied to alloy steels. The methods which involve weighing as barium sulfate are tedious and much too slow to serve as control of a steel-making operation; the various modifications of the long-used evolution method are somewhat lacking in accuracy, especially when applied to highly alloyed steels, and leave much to be desired in point of speed. Seeking a better method, the authors decided to investigate the determination of sulfur by combustion of the steel in oxygen as holding the best promise of meeting the requirements, but found, although a number of papers on this general procedure had been published, that considerable additional study with careful attention to details of procedure was required before they could regard the method as reasonably satisfactory.

A routine method for the simultaneous determination of sulfur and carbon in steel by combustion in oxygen was reported by Holthaus (3), following work published by Schmitz (10) and Vita (14). Since that time several other papers (1, 2, 6, 11-13, 15) have appeared dealing mainly with details of the final absorption of the sulfur oxides formed in the combustion, and of the method of titrating or otherwise estimating the amount of sulfur absorbed. These papers, however, consist largely of accounts of special procedures, and of tables of comparative results by combustion and gravimetric methods; they do not give a thorough discussion of precise conditions which the authors' experience leads them to believe are necessary for best recovery of the sulfur. Further, since most of the results reported appear to be based on some empirical titration factor, obtained from standard steels, the necessary conditions cannot be inferred from the published details of procedure. Indeed, the apparent use of an empirical factor leads one to believe that the method as it has been used yields only some reasonably constant percentage of the sulfur present but not all of it. The authors' investigation indicates that not only is this true, except perhaps for certain special and rather impractical conditions, but that the conditions requisite to a consistent high percentage recovery must themselves be precisely defined and carefully adhered to. Nor is this surprising, for in a 1.6-gram sample of a steel containing 0.05 per cent of sulfur there is only 0.8 mg. of sulfur. The precautions necessary for an accurate determination of this small amount may be inferred from the fact that the retention anywhere within the combustion tube or in the path of the gas to the absorbing liquid, of even 0.1 mg.

of sulfur dioxide, corresponds to an error of 0.003 per cent on the sulfur or 6 per cent of the sulfur present.

The first essential is the complete combustion and liberation of the sulfur. A high temperature is necessary, ranging from a minimum of 1200° to 1425° C., depending upon the nature of the steel. The authors have found that a steel which gives up all its sulfur in 10 or 12 minutes when burned at 1200° C. in oxygen liberates only some 75 per cent at 1100° C. The temperature must be higher for the more highly alloyed steels; it may be reduced somewhat by the use of metallic tin as a flux. The temperature suitable for various types of steels is listed in Table I; at these temperatures, which are recommended as the result of a considerable number of experiments and include a factor of safety, practically all the sulfur from the steel sample is evolved within a period of 10 or 12 minutes.

Combustion technic in this country, as applied to the determination of carbon in steel, makes use of a refractory bedding, usually alumina, to protect the boat from the molten oxides formed by the combustion. This practice does not permit of complete liberation of the sulfur, which may be held chemically by traces of alkali or mechanically in gas pockets in the melt. All bedding materials which the authors have tried hold back sulfur. Alumina is particularly bad in this respect; its ability to fix sulfur compounds was noted by Isham and Aumer (4) in 1908 and by Rooney (9) in 1934, and this probably explains the very long heating period found necessary by Kar (5). Since a bedding to protect the boat would be desirable if it could be used, the authors have tried a number of materials including alundum, chrome ore, chromic oxide, ferric oxide, ferrous oxide, magnesite, stannic oxide, c. p. silica, Ottawa sand, various mesh sizes of broken boat material, mullite, titania, manganese dioxide, kaolin, clay, and zirconia sand. Zirconia sand is one of the least objectionable, but because of gas pocket formation cannot be used except on a very small sample (such as 0.3 gram) and even then requires 1300° C. for a plain carbon steel which could be run successfully at 1200° C. without bedding.

If no bedding is used, the boat must be discarded after a single combustion; this, however, can be done at comparatively small expense. The boat must not absorb sulfur, must be sufficiently inert to the molten oxides to protect the combustion tube, and must withstand the high temperature of combustion. After all the boats ordinarily used heretofore and all obtainable on the market had been tried, unglazed porcelain boats fulfilling all these requirements were

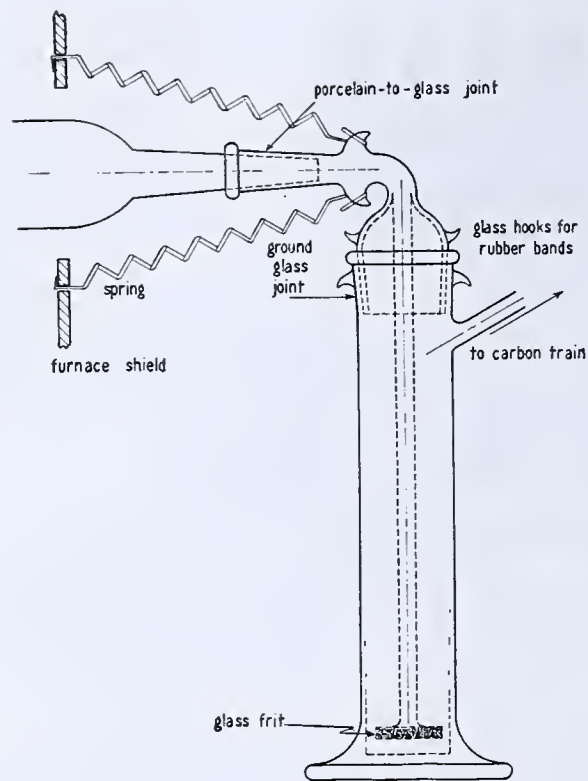


FIGURE 1. DETAIL OF ABSORPTION VESSEL

finally obtained through the coöperation of the McDanel Refractory Porcelain Company.

Some writers have recommended the use of a plug at the exit end of the combustion tube to hold back the finely divided iron oxide produced by the rapid combustion of the steel. The authors have been unable to find any plug which does not retain some of the sulfur oxides, and consequently use none. In any case they believe that a plug is unnecessary, for repeated trials have shown that the fume, even when it passes through the absorbing solution, does not affect the precision or reproducibility of the titration, provided that the oxygen flow is maintained at the maximum rate permissible through the absorption vessels and the conditions of combustion are the optimum for the evolution of the sulfur. The fume consists not only of iron oxide but also of other oxides, and varies both in amount and composition with the type and kind of steel. The glass frit in the absorption vessel may in time become clogged by the fume; if so, it is readily cleaned by rinsing in warm dilute hydrochloric acid and subsequent repeated washings with water.

To ensure the quantitative removal of sulfur from the combustion tube, there should be no cool exit end at which sulfur trioxide might be adsorbed. The authors maintain this end at about 200° C. by keeping it close to the heating zone of the furnace. To withstand this temperature and avoid the use of rubber, which readily absorbs sulfur dioxide, the tube is connected to the absorption vessel by a ground porcelain-to-glass joint. This joint, which can be made by a good glass-blower, serves its purpose very well; it is gas-tight at the pressure used, yet easily disconnected, an arrangement of springs ensuring against accidental disconnection.

Absorption of the sulfur oxides at the speed of oxygen flow needed for rapid combustion has been attempted by various devices ranging from straight tubes to a special spray apparatus (8). Sulfur dioxide is absorbed with no particular difficulty; sulfur trioxide is present in smaller amounts but tends to form a mist which may pass through the usual absorption devices. A glass frit effects the absorption of both gases satisfactorily and is convenient to use. (The authors use a Jena frit, porosity G1, nominal pore diameter 100 to 120 microns.) The absorbing solution is a dilute neutral

hydrogen peroxide. Estimation of the sulfuric acid formed in this solution offers no difficulty; care must be taken, but by a proper choice of indicator, volume, and lighting, the end point can be noted to an accuracy of 0.05 ml. of 0.01 *N* sodium hydroxide, corresponding to 0.0005 per cent of sulfur on a 1.6-gram sample of steel.

The facts summarized above were discovered experimentally by a process of successive elimination of the several sources of error, a procedure which proved to be unavoidable and required a great number of analyses of standard samples of steels of every type obtainable. Even with all these precautions the results tend to be low, though consistent with one another. By washing out the combustion tube after a considerable number of samples have been burned, the authors found that some sulfur is retained in it, though none seems to be retained by the boat as used. The amount retained in the tube seems insufficient to account for the difference between the authors' results and the accepted values. In any case, the results on ordinary steels of low and medium sulfur content are sufficiently accurate for practical purposes, and on any steel are consistent even though they may be low by about 8 per cent of the accepted value on steels of the highest sulfur content. In view of its consistency, the method may safely be used on any steel by use of a factor established by comparison with a series of analyses of a standard similar in type to the sample; and it is especially suitable for high-alloy steels (generally of low sulfur content) which resist solution in acid.

Apparatus and Reagents

The apparatus for determining sulfur, either alone or in conjunction with carbon, closely resembles the usual carbon combustion train. In the sulfur determination, however, few variations in apparatus or procedure are permissible. Certain parts are of special design, others must be made of certain materials only; therefore the whole assembly is described piece by piece and in detail. The apparatus can be purchased complete as a unit or parts may be ordered separately.

OXYGEN SUPPLY. The oxygen used should be not less than 99.5 per cent pure and should be free from carbon monoxide, carbon dioxide, or any other acidic or carbon-bearing material. If oxygen of this grade cannot be obtained, special provision must be made to purify it. Reducing valves must be used to step the cylinder pressure down to not more than 10 cm. of mercury and permit a steady controlled flow of gas through the train. Several different types of valves suitable for this purpose are readily obtainable. It is convenient to insert a bubbler containing sulfuric acid to indicate the rate of flow.

OXYGEN PURIFYING TRAIN. With oxygen of the purity specified above, there is no need of the purifying train; nevertheless, as a precaution it is customary to insert a carbon dioxide absorbent, such as soda lime, followed by calcium chloride. It is convenient to have attached to the inlet side of the train a reservoir, acting as a pressure regulator, from which an auxiliary supply of oxygen is drawn during the actual combustion.

MERCURY TRAP OR MANOMETER. Either may be used; the mercury trap is preferred by some, as it serves not only to indicate the pressure roughly, but also to prevent back flow of gas.

ELECTRIC FURNACE. For the temperatures needed (1200° to 1425° C.) the authors have used a type of resistance furnace with replaceable silicon carbide rods, which operates on 110 or 220 volts, alternating or direct current, and has proved entirely satisfactory for this work. (The authors have used a high-temperature carbon combustion furnace with replaceable Globar elements, controlled by a carbon rheostat, all furnished by the Burrell Technical Supply Co.) It is about 35 cm. (14 inches) long, 30 cm. (12 inches) outside diameter, and takes a tube 5 cm. (2 inches) in diameter. A new furnace should be heated slowly to the operating temperature, as very rapid heating may cause the refractory to crack and spall from the outer insulating material. The furnace withstands continuous service at 1400° C. indefinitely; the useful life of the heating elements is from 1 to 3 months.

TEMPERATURE CONTROL. Some means of controlling the temperature is desirable, as a temperature above that needed for a

given steel causes unnecessary wear and tear on the combustion tube and furnace. Control of the heating current is accomplished simply by a suitable rheostat in series with the furnace. Such a rheostat must be capable of carrying nearly 30 amperes; any type meeting this requirement and affording flexible control will do. Carbon plate resistors accomplish stepless regulation of current; the more common plate type of laboratory rheostat is not as flexible, but, in case no ammeter is available to indicate the current flow, the approximate value may be judged by the position of the contact arm if the voltage may be assumed to remain constant.

The temperature is measured by use of a noble metal thermocouple whose hot junction is placed at the middle of the heating chamber as close to the combustion tube as is practicable. It is well to check the temperature of this position against that inside of the tube by sighting an optical pyrometer on a heated boat in the combustion position while noting the temperature indicated by the thermocouple. Automatic control is easily applied and is to be recommended wherever the amount of work to be done justifies the expense.

COMBUSTION TUBE. Only an unglazed, vitrified tube of porcelain may be used; other commercial types are either affected by the high temperature or tend to react to some extent with the sulfur dioxide evolved. The tube life should be as long as is usual in the case of carbon determinations. As to size, a tube 2.6 cm. (1.125 inches) inside diameter and 68 or 70 cm. (27 or 28 inches) in length has been found most satisfactory, though the length may be reduced to 62.5 cm. (25 inches) if suitable provision is made for keeping the intake end reasonably cool. The exit end is connected to the absorption vessel by a ground porcelain-to-glass joint. By carefully standardizing the taper and grinding of the two tubes, the parts have been made interchangeable so that a gas-tight joint is secured between any combustion tube connected to any standard absorber. The joint is seated and held firmly in place by means of spiral springs anchored to the safety shield of the furnace and ending in hooks which slip over lugs on the inlet tube of the absorber. Details of this connection are shown in Figure 1.

COMBUSTION BOAT. The boat material must be carefully selected. The shape also is designed to permit easy evolution of the sulfur; the boats are rectangular in plan with length 10 cm. (4 inches), width 2 cm. (0.8 inch), and depth 1 cm. (0.4 inch), outside dimensions. The walls are thin and at right angles to the flat bottom, affording a large bottom surface upon which the sample can be thinly spread in a single layer.

ABSORPTION VESSEL. This vessel 20 cm. (8 inches) in height and 3 cm. (12 inches) in diameter, shown in Figure 1, consists of an inlet tube, connected through the interchangeable ground joint with the combustion tube, sealed to a glass frit (Jena G1), which breaks the gas stream into a cloud of small bubbles, thus effecting complete absorption of the sulfur dioxide and sulfur trioxide in the solution in the vessel. The inlet tube enters the absorption vessel through a ground-glass joint, so that the gas passing through this vessel may be forced without loss through the train for carbon absorption. The solution is rendered distinctly acid by absorption of the sulfur gases, and retains none of the carbon dioxide, even that which would normally dissolve being swept out by the stream of carbon dioxide-free oxygen passed after the combustion is complete.

REAGENTS. The 0.5 per cent hydrogen peroxide solution must be made by dilution with carbon dioxide-free water. A convenient strength for the sodium hydroxide solution is 0.01 *N*; this also must be made up and kept free of carbon dioxide. It is well to have at hand 0.01 *N* acid for back-titration or for deliberate adjustment of an end point.

Procedure

DETERMINATION OF SULFUR ALONE. First make sure that the sulfur absorber is perfectly clean and otherwise in good condition. If the frit or vessel appears to contain much oxide fume, add a little warm 1 to 1 hydrochloric acid through the intake tube, then rinse thoroughly with distilled water until the washings are neutral to the methyl red indicator. Transfer to the absorber 50 ml. of a 0.5 per cent hydrogen peroxide solution (prepared by diluting 17 ml. of 30 per cent hydrogen peroxide to 1000 ml. with carbon dioxide-free water) and add 2 to 3 drops of methyl red indicator, prepared by dissolving 0.1 gram of methyl red in 60 ml. of 85 to 95 per cent alcohol and diluting to 100 ml. with carbon dioxide-free water. If the solution is red in color, as it generally is, owing to a trace of acid in the peroxide, add 0.01 *N* carbonate-free sodium hydroxide solution dropwise until one drop just dispels the red color; this is taken as the end point. If this point is overtitrated, add one or more drops of 0.01 *N* carbon dioxide-free acid, and adjust to the end point with the standard sodium hydroxide solution.

Next transfer 1.6 grams of the steel sample (0.8 gram, if sulfur is over 0.3 per cent) to a clean new combustion boat, spreading the drillings or chips over the bottom so that they lie as nearly as possible in a single layer. If tin is required as an accelerator, spread 0.15 to 0.2 gram of tin shot (20-mesh) over the sample, distributing it as evenly as possible.

Push the boat into the combustion tube for a distance of 5 to 7 cm. (2 to 3 inches), and attach the sulfur absorber to the exit end of the tube, making sure that all parts are held firmly together by the rubber bands and the coil springs provided for the purpose. Finally, push the boat into the hottest zone of the tube, insert the stopper, and turn on the oxygen to flow at the rate of about 300 ml. per minute. Continue to admit the oxygen at this rate for 10 minutes. The solution in the sulfur absorber will suddenly turn red in color as the evolved sulfur dioxide reaches it. When sufficient time has elapsed to sweep all the sulfur gases out of the tube, turn off the oxygen and disconnect the absorber; if its temperature has been noticeably raised, place it in running water to cool. Then pull the boat out of the furnace and discard it; in removing the boat do not let it rest in the cold end of the tube as it may crack the tube, but pull it out at one stroke and without a stop on to the receiving tray held just under and in front of the opening.

Using the glass frit with its delivery tube as a plunger, add the 0.01 *N* sodium hydroxide solution until the red color just disappears. Rinse the frit three times through the inlet end of the tube by means of a stream of carbon dioxide-free water from a wash bottle, adding the rinsings to the solution in the absorber, and once more add the standard sodium hydroxide solution to the disappearance of the red color. Finally raise the frit over the surface of the liquid, allow it to drain, and complete the titration if the red color reappears. If the solution is exactly 0.01 *N* and 1.6 grams of sample were used, the number of milliliters used gives the sulfur in hundredths of one per cent. Otherwise, multiply the number of milliliters used by the sulfur titer of the solution, multiplied by 100, and divide by the weight of sample used.

The titrated solution is poured from the absorber and replaced with another 50 ml. of the hydrogen peroxide solution preparatory to another determination. No rinsing of the absorber is necessary except after cleaning with acid.

MINIMUM COMBUSTION TEMPERATURE FOR DIFFERENT STEELS. It is desirable to operate at the lowest temperature possible to prolong the useful life of the tube and heating elements. The exact temperature necessary varies somewhat with the kind of steel being analyzed and the time available for continuing the stream of oxygen through the train. If no tin or other accelerator is used, the lowest safe operating temperatures and other operating data for a number of steels are given in Table I.

TABLE I. MINIMUM COMBUSTION TEMPERATURE

Kind of Steel	Wt. of Sample Grams	Lowest Safe Temperature		Total Time of Passing O ₂	
		° C.	° F.	O ₂ Flow ML./min.	Min.
Plain carbon	1.6	1200	2200	250	12
Low alloy	1.6	1260	2300	250	12
18-8	1.6	1340	2450	250	12
25% chrome	1.6	1400	2550	250	12
High-speed tool	1.6	1370	2500	250	12

These temperatures are satisfactory for the sulfur determination without the use of tin, but for complete carbon elimination tin shot should be added to samples of the last four types. This use of flux also permits a somewhat lower combustion temperature for sulfur liberation, thus conserving heating elements and combustion tube. Hence the addition of tin and a temperature of 1300° to 1350° C. are recommended for steels containing more than 20 per cent of chromium or more than 30 per cent of total alloying elements.

At these temperatures combustion of the steel is complete within 3 minutes after pushing the boat into the hot zone and turning on the oxygen. The rest of the time is required to sweep the sulfur dioxide and carbon dioxide completely into the absorption vessel, this depending upon the maximum flow that can be maintained. The maximum flow in turn depends upon the porosity and condition of the bubbler in the sulfur absorber, and on the method used for

TABLE II. DETERMINATION OF SULFUR ALONE

Standard Employed	Certificate Value of Standard, Sulfur			Value Obtained by Combustion as Described, Sulfur				
	No. of analyses	High %	Low %	Average %	No. of analyses	High %	Low %	Average %
U. S. Steel Corp.								
Standard K, plain steel	25	0.121	0.104	0.114	11	0.111	0.101	0.106
Standard L, plain steel	25	0.064	0.056	0.059	9	0.059	0.053	0.056
Bureau of Standards Standard Sample								
35a, plain steel ^a	17	0.039	0.030	0.037	2	0.044	0.044	0.044
16b, plain steel	15	0.032	0.028	0.031	1	0.033
9c, plain steel	21	0.040	0.034	0.036	1	0.036
16c, plain steel	21	0.046	0.039	0.044	3	0.043	0.042	0.042
13c, plain steel	14	0.025	0.020	0.023	1	0.023
20c, plain steel	16	0.028	0.024	0.026	1	0.028
8d, plain steel	18	0.088	0.081	0.083	12	0.078	0.075	0.077
55, ingot iron	14	0.019	0.014	0.017	4	0.017	0.015	0.016
50, W 17.56, V 0.756, Cr 3.61	12	0.034	0.026	0.031	17	0.033	0.030	0.031
73, Cr 13.93, Ni 0.072, Si 0.360	17	0.034	0.027	0.031	2	0.027	0.027	0.027
101, 18-8 steel	20	0.015	0.010	0.013	21	0.012	0.010	0.011
105, special high sulfur, not standard for sulfur				About 0.6	4	0.54	0.52	0.53

^a Bureau of Standards does not recommend this steel as a standard for sulfur by evolution method.

determining the carbon. In the gravimetric method for carbon the maximum flow through the bubbler governs; in the volumetric method the maximum flow permissible through the carbon dioxide absorption bulb is the controlling factor.

SIMULTANEOUS DETERMINATION OF SULFUR AND CARBON. Since this type of sulfur absorber removes all oxides of sulfur (as found by direct trial) carbon may be determined simultaneously by leading the gases from it through a carbon absorption train arranged for either the volumetric or the gravimetric determination of carbon. For the gravimetric determination of carbon it is essential that the concentration of water vapor in the gases entering the carbon-absorption bulb be controlled so that no appreciable amount of water is either yielded to, or abstracted from, that bulb. This can be done by use of a sulfuric acid bubbler, followed by a tower containing the identical desiccant used in the carbon-absorption bulb. The type of bubbler described by Lundell, Hoffman, and Bright (?) is convenient, as it readily permits the acid to be changed after each run without disconnection of the tower. If the carbon is to be determined volumetrically and is under 0.60 per cent, use 1.6 grams of sample; if more than 0.60 per cent carbon is expected, use 0.8 gram of sample. If the carbon is to be determined gravimetrically, 1.6 grams of sample may be used for all steels containing less than 0.3 per cent of sulfur, regardless of the percentage of carbon present.

DETERMINATION OF SELENIUM SIMULTANEOUSLY WITH SULFUR AND CARBON. In the method as described selenium is evolved as SeO_2 . Unfortunately the selenium dioxide begins to sublime at 250°C . and, consequently, condenses in the cooler portion of the combustion tube. Research is now being carried on with a view to devising a method which will permit the determination of selenium as well as sulfur and carbon. The work done so far looks very promising and indicates that a solution of the problem in the near future may be anticipated.

Results

Some typical results on a variety of steels are presented in Tables II and III, all obtained by following the exact procedure described above, which show that this analytical method is capable of yielding consistent results, either for sulfur alone or for sulfur and carbon simultaneously.

It is to be noted that these results are nearly always somewhat lower than the accepted standard values, the difference being greater the higher the sulfur content. A part of this difference arises from the fact that a trace of the sulfur gases is retained within the combustion tube. Another possible source of slight error is that the combustion of the steel under the authors' conditions sometimes produces a slight fume, visible in the absorption vessel, the amount varying from one steel to another, and that this fume may in effect fix a trace of the sulfur oxides. The authors have, however, been unable to establish this effect, and mention this possibility merely because the results on one steel, which evolved a larger amount of fume, appeared to be relatively lower, in comparison to the accepted values, than those on the other steels. It is their present belief that these two sources of error do not suffice to account for the differences between their results obtained by the combustion method and the accepted values, and that the reason for these differences can be discovered only by further careful investigation both of the combustion method and of the methods by which the accepted values were obtained. In the meantime it seemed worth while to publish this study of the method, which in any case is satisfactory for steels of low sulfur content, and particularly for high-alloy steels which are not easily analyzed for sulfur by other methods.

Summary

The apparatus and procedure are described in detail for the determination, within 15 minutes, of sulfur or of sulfur and

TABLE III. SIMULTANEOUS DETERMINATION OF SULFUR AND CARBON

Standard Employment	Certificate Value of Standards Employed								Values Obtained by Combustion						
	Carbon				Sulfur				Carbon			Sulfur			
	No. of analyses	High %	Low %	Average %	No. of analyses	High %	Low %	Average %	No. of analyses	High %	Low %	Average %	High %	Low %	Average %
Bureau of Standards, 13c, plain steel	9	0.583	0.569	0.573	14	0.025	0.020	0.023	5	0.582	0.563	0.572 ^a	0.020	0.020	0.020
Bureau of Standards, 50, alloy steel, W 17.56, V 0.756, Cr 3.61	13	0.682	0.630	0.656	12	0.034	0.026	0.031	5	0.680	0.665	0.671 ^b	0.031	0.030	0.030
Bureau of Standards, 101, 18-8 steel	13	0.064	0.058	0.063	20	0.015	0.010	0.013	2	0.065	0.060	0.063 ^b	0.012	0.010	0.011
Standard B, plain steel	3	0.109	3	0.031	10	0.110	0.102	0.106 ^b	0.033	0.026	0.030
Bureau of Standards, 105, special high-sulfur, provisional certificate	0.193				About 0.6	1	0.21 ^a	0.52

^a Carbon determined volumetrically.

^b Carbon determined gravimetrically.

carbon simultaneously, in all kinds of steels, by combustion of the steel in oxygen at a high temperature. The results for sulfur are slightly lower than the values commonly accepted as correct, but are consistent and reproducible and satisfactorily accurate for most practical purposes, particularly in high-alloy steels containing little sulfur.

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The Dextrose-Levulose Ratio and the Polarizing Constants of Raw Cane Sugars

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UNTIL recently the only practical method for the determination of dextrose and levulose in raw sugars was that of Browne (1), based on the difference between sucrose, S , and direct polarization, P , and the total reducing sugars, R . The ratio between $S - P$ and R has been termed the "polarizing constant." The numerical value of the constant is about 0.3 when the reducing sugars consist of dextrose and levulose in equal proportions, varies inversely with the dextrose-levulose ratio, and becomes negative when this ratio rises above 64 to 36.

To calculate the percentages of dextrose and levulose in a raw sugar from $S - P$ and R , Browne makes use of Equations 1 and 2:

$$x + ky = R \quad (1)$$

$$cx + c_1y + S = P \quad (2)$$

where x and y are the percentages of dextrose and levulose, respectively, k is the reducing ratio of levulose to dextrose, c the polarizing ratio of dextrose to sucrose at 20° C., c_1 that of levulose to sucrose, R the percentage of total reducing sugars, expressed as dextrose, P the direct polarization of the normal weight solution at 20° C., and S the percentage of sucrose found by inversion with invertase.

Solving the equations for x and y ,

$$y = \text{percentage of levulose} = \frac{cR + S - P}{kc - c_1}$$

$$x = \text{percentage of dextrose} = R - ky$$

The numerical value of c is 52.74 : 66.5 = 0.793, that of c_1 is -92.88 : 66.5 = -1.397. The latter varies somewhat with concentration and temperature, but in practice only the temperature correction needs to be considered, and it is best to make all polarizations at exactly 20° C. For k an average value of 0.915 may be used if Allihn's method of reducing sugar determination is employed.

Applying this method to the analysis of mixtures of pure sugars, Browne found that it gives very good results when the ratio between sucrose and reducing sugars is low. But when the ratio is high, as in raw sugars, the difference between the sucrose and the direct polarization becomes very small, and any error in the polarimetric readings has a large effect on the percentages of dextrose and levulose found, especially if the errors in the two readings happen to be in the opposite direc-

tion. In one experiment, with a mixture of 98 per cent of sucrose and 1 per cent each of dextrose and levulose, Browne found 0.75 per cent of dextrose and 1.17 per cent of levulose—that is, a percentage ratio of 39.1 between dextrose and total reducing sugars, instead of 50.

In 1934 Zerban and Wiley (4) published a new method for the determination of dextrose and levulose in the presence of large amounts of sucrose, extending previous work by Jackson and Mathews (3) to the analysis of raw sugars. The total reducing sugars are determined by the method of Lane and Eynon, and the levulose is determined by selective reduction of a modified Ost's solution at 55° C. A table of Lane and Eynon factors for 10 ml. of Soxhlet solution and for mixtures of dextrose and levulose in all possible proportions, in the presence of 10 or 25 grams of sucrose, has been given by Zerban and Wiley (4), as well as a method for calculating the percentages of dextrose and of levulose, by successive approximations. The calculation may be shortened materially by the use of Equations 3 and 4:

$$ax + y = R \quad (3)$$

$$0.0806 x + y = R_1 \quad (4)$$

where x and y are the milligrams of dextrose and levulose, respectively, in 100 ml. of solution analyzed. R represents milligrams of total reducing sugars, expressed as levulose, in 100 ml. of solution. It is calculated, as usual, by multiplying the Lane and Eynon factor in Table I by 100, and dividing by the titer found. a is the varying reducing ratio between dextrose and levulose, and is also given in Table I. R_1 is the milligrams of apparent levulose in 100 ml. of solution, found by the method of Jackson and Mathews, and corrected for the reducing effect of the sucrose. The factor 0.0806 is the constant reducing ratio of dextrose to levulose in the method of Jackson and Mathews, 12.4 mg. of dextrose having the same reducing effect as 1 mg. of levulose.

Solution of Equations 3 and 4 gives

$$x = \text{mg. of dextrose in 100 ml. of solution} = \frac{R - R_1}{a - 0.0806}$$

$$y = \text{mg. of levulose in 100 ml. of solution} = R - ax$$

The values of the denominator, $a - 0.0806$, are also included in Table I.

TABLE I. LANE AND EYNON FACTORS AND REDUCING RATIOS FOR DETERMINATION OF DEXTROSE AND LEVULOSE IN RAW SUGARS

10 Grams of Sucrose				25 Grams of Sucrose			
Titer	Lane and Eynon factor	Reducing ratio, a	$a - 0.0806$	Titer	Lane and Eynon factor	Reducing ratio, a	$a - 0.0806$
15	48.1	1.0434	0.9628	15	44.7	1.0419	0.9613
16	48.0	1.0430	0.9624	16	44.6	1.0396	0.9590
17	47.9	1.0426	0.9620	17	44.4	1.0375	0.9569
18	47.9	1.0422	0.9616	18	44.3	1.0356	0.9550
19	47.8	1.0418	0.9612	19	44.1	1.0339	0.9533
20	47.7	1.0414	0.9608	20	44.0	1.0324	0.9518
21	47.6	1.0410	0.9604	21	43.9	1.0311	0.9505
22	47.5	1.0406	0.9600	22	43.8	1.0300	0.9494
23	47.5	1.0402	0.9596	23	43.7	1.0290	0.9484
24	47.4	1.0398	0.9592	24	43.6	1.0281	0.9475
25	47.3	1.0394	0.9588	25	43.5	1.0273	0.9467
26	47.2	1.0390	0.9584	26	43.4	1.0266	0.9460
27	47.1	1.0386	0.9580	27	43.3	1.0260	0.9454
28	47.1	1.0382	0.9576	28	43.2	1.0255	0.9449
29	47.0	1.0378	0.9572	29	43.1	1.0251	0.9445
30	46.9	1.0374	0.9568	30	43.0	1.0248	0.9442
31	46.8	1.0370	0.9564	31	42.9	1.0247	0.9441
32	46.8	1.0366	0.9560	32	42.9	1.0247	0.9441
33	46.7	1.0362	0.9556	33	42.8	1.0246	0.9440
34	46.7	1.0358	0.9552	34	42.7	1.0246	0.9440
35	46.6	1.0354	0.9548	35	42.6	1.0246	0.9440
36	46.6	1.0350	0.9544	36	42.6	1.0245	0.9439
37	46.5	1.0346	0.9540	37	42.5	1.0245	0.9439
38	46.5	1.0342	0.9536	38	42.5	1.0245	0.9439
39	46.4	1.0338	0.9532	39	42.4	1.0245	0.9439
40	46.4	1.0334	0.9528	40	42.3	1.0245	0.9439
41	46.4	1.0330	0.9524	41	42.2	1.0244	0.9438
42	46.3	1.0326	0.9520	42	42.1	1.0244	0.9438
43	46.3	1.0322	0.9516	43	42.1	1.0244	0.9438
44	46.2	1.0318	0.9512	44	42.0	1.0244	0.9438
45	46.2	1.0314	0.9508	45	41.9	1.0244	0.9438
46	46.2	1.0313	0.9507	46	41.8	1.0243	0.9437
47	46.2	1.0312	0.9506	47	41.7	1.0243	0.9437
48	46.1	1.0312	0.9506	48	41.7	1.0243	0.9437
49	46.1	1.0311	0.9505	49	41.6	1.0243	0.9437
50	46.1	1.0311	0.9505	50	41.5	1.0243	0.9437

There is a small error in the final result for dextrose and levulose, because the reducing ratio between the two sugars varies not only with the concentration of either present alone, but slightly also with the proportion between the two, but this error does not exceed 0.23 per cent of the final results. In the analysis of mixtures containing 0.5 to 1.5 per cent of total dextrose and levulose, the remainder being sucrose, the maximum experimental error was found to cause a change of only 2 units in the percentage ratio between dextrose and total reducing sugars, considerably less than in the older method based on combined polarimetric and reduction measurements. The mean error was only ± 1.0 unit. However, when mixtures with a high proportion of reducing sugars and only small quantities of sucrose are to be analyzed, the older method will give more reliable results because the error in the reducing sugar determinations becomes greatly multiplied.

When either of the two methods described is applied to the analysis of raw sugars, other sources of error arise, due to the presence of nonsugars which may be optically active or have copper-reducing power, and possibly of other reducing sugars besides dextrose and levulose. Optically active impurities will alter the direct polarization, although they do not affect the sucrose value, provided that invertase is used for hydrolysis. The impurities are at least partially removed by proper clarification. The polarization after deleading must be used for P , and not the direct polarization in the presence of excess lead. It is necessary, therefore, to delead the entire filtrate from the lead precipitate, and to determine P and S in the resulting solution. Under these circumstances the volume of the lead precipitate does not affect the difference between S and P .

Clarification

There is considerable difference of opinion with regard to clarification prior to reducing-sugar determinations. Some writers maintain that treatment with neutral lead acetate is necessary in order to remove reducing nonsugars; others have

not been able to find such nonsugars in cane products, and even advise against the use of lead acetate because it may precipitate reducing sugars. There is general agreement, however, that it is necessary to remove calcium salts and also any excess of lead if used. The safest way probably is to clarify with a minimum of neutral lead acetate, and to remove the excess lead. This procedure has been used in the present investigation, dry potassium oxalate being added to the filtrate from the lead precipitate to remove both lead and calcium.

Because of our meager knowledge of the errors caused by the impurities still remaining after clarification, it is impossible to tell definitely which of the two methods may be expected to give more reliable results in the analysis of actual sugar products. This will depend in a large measure on the purity of the material to be analyzed. The results obtained with mixtures of pure sugars would indicate that the method combining polarization and reducing power is preferable for low-purity products that are high in reducing sugars. In the case of high-purity products with low content of reducing sugars, the amount of reducing nonsugars is probably small in comparison to the total reducing sugars. Furthermore, if two copper-reduction methods are combined, the effect of the presence of other reducing substances besides dextrose and levulose may be expected to be similar in both.

Application of Methods

The errors in polarimetric measurements may be greatly reduced by the use of modern high-precision equipment, and in individual cases the choice between methods will be determined by the apparatus available. The limitations of all combined methods must always be kept in mind in the interpretation of results.

Both methods described above have been applied to the analysis of 100 typical raw sugars received by the New York Sugar Trade Laboratory during the past 2 years. These included 33 samples from Cuba, 21 from Puerto Rico, 15 from the Philippines, 10 from Hawaii, 9 from Santo Domingo, and 12 from miscellaneous sources. It is usually not known how much time has elapsed between the manufacture of a given sugar and its discharge at mainland ports. For this reason the results obtained reflect merely the composition of the sugar after arrival at its destination, and not in its original state. There were two samples, however, which were known to have been stored for at least one year, and the results obtained with these are discussed separately (Table VI).

In order to save space, the results are not given in full, but some typical examples are shown in Table II. The method combining polarization and reducing power is designated as I, and that based on two different copper-reduction methods as II. The polariscopic work was done by C. A. Gamble; the reducing sugar determinations in the first half of the samples were made by M. H. Wiley, in the second half by Carl Erb.

TABLE II. ANALYSES OF SOME INDIVIDUAL SAMPLES

No.	Method I			Method II		
	R^a	$D\%$ R^b	$(S - P)/R^c$	R^a	$D\%$ R^b	$(S - P)/R^c$
66	1.55	55.5	0.181	1.55	55.7	0.175
67	1.40	41.9	0.480	1.39	47.1	0.366
83	0.73	47.5	0.358	0.73	44.6	0.425
91	0.73	45.1	0.412	0.73	41.8	0.478
16	0.88	51.5	0.273	0.88	51.0	0.273
24	1.06	48.8	0.330	1.06	52.3	0.255
32	1.23	51.5	0.268	1.23	47.0	0.366
43	1.16	49.6	0.311	1.15	44.9	0.348
6	0.61	45.0	0.413	0.60	49.8	0.315
37	1.03	56.2	0.166	1.03	54.8	0.195
54	1.12	46.2	0.386	1.10	56.4	0.155
47	0.94	65.7	-0.043	0.94	59.1	0.106

^a Per cent of total reducing sugars found.

^b Percentage ratio of dextrose to total reducing sugars.

^c Polarizing constant; in method II calculated from dextrose and levulose found.

The differences between the results obtained by the two methods, in terms of the ratio of dextrose to total reducing sugars, are summarized in Table III, for all 98 cases.

TABLE III. DIFFERENCES IN PERCENTAGE RATIOS OF DEXTROSE AND TOTAL REDUCING SUGARS, FOUND BY THE TWO METHODS

Difference in Ratio	Cases
Within 1 unit	11
Within 2 units	25
Within 3 units	32
Within 4 units	38
Within 5 units	48
Within 6 units	64
Within 7 units	69
Within 8 units	76
Within 9 units	81
Within 10 units	86
Within 11 units	92
Within 12 units	94
Within 14 units	95
Within 16 units	96
Within 18 units	97
Within 19 units	98

In many cases the ratio of dextrose to total reducing sugars found by method I agrees closely with that obtained by method II, but in others there are considerable divergences, amounting in four cases to more than 12 units, with a maximum of 18.4. Corresponding differences are found in the polarizing constants.

The total range of the percentage ratio of dextrose to total reducing sugars was found to be from 32.6 to 67.4 for method I, and from 35.3 to 65.6 for method II. The range of the polarizing constant was from -0.079 to 0.683, and from -0.040 to 0.628, respectively. However, the average ratios were practically the same (50.4 by method I, 50.7 by method II), and likewise the polarizing constants (0.293 by method I, 0.285 by method II), indicating that the errors in the two methods are merely due to experimental difficulties, and not of a systematic nature. The discrepancies between the two methods in individual cases may be caused partly by the fact that in method I the determinations are made on separate portions of a sample, one clarified with lead subacetate and the other with neutral lead acetate, while in method II only one solution is prepared, clarified with neutral acetate, and both determinations are made on aliquots of the same filtrate.

The average dextrose ratio for all the sugars is practically that of invert sugar. The extent of the deviations from the 50:50 ratio between dextrose and levulose is summarized in Table IV for both methods.

TABLE IV. EXTENT OF DEVIATIONS

Ratio	Number of Cases	
	Method I	Method II
Between 49 and 51	8	24
Between 48 and 52	22	31
Between 47 and 53	28	46
Between 46 and 54	40	58
Between 45 and 55	52	63
Between 44 and 56	60	73
Between 43 and 57	66	84
Between 42 and 58	75	85
Between 41 and 59	83	89
Between 40 and 60	86	92
Between 32 and 68	98	98

Taking method II as the basis, the ratio of dextrose to total reducing sugars is within 40 to 60 per cent in all but six cases, and between 45 and 55 per cent in nearly two-thirds of all samples. Even in extreme cases the amount of levulose is only about twice that of the dextrose, or vice versa. According to method I, the deviations from the 50 per cent ratio are somewhat larger.

The average dextrose-ratio and polarizing constants for each of the geographical districts represented by nine or more samples are shown in Table V.

Table V shows that even for single geographical districts the average ratio between dextrose and levulose does not deviate much from that for invert sugar. The average polarizing constants vary from about 0.02 to 0.4, method II giving a some-

what narrower range than method I. For both Santo Dominican and Philippine sugars method I gives a higher average polarizing constant than method II. It is interesting to note in this connection that many years ago Browne (2), using the Herzfeld method of sucrose determination, also found low polarizing constants, around 0.2, for the Philippine mat sugars of that time, while Cuban sugars gave constants of about 0.35.

TABLE V. AVERAGE DEXTROSE-RATIO AND POLARIZING CONSTANTS

	Method I		Method II	
	D/R %	(S - P)/R	D/R %	(S - P)/R
Cuba	49.7	0.305	47.8	0.348
Puerto Rico	53.7	0.221	51.9	0.256
Santo Domingo	45.8	0.394	49.7	0.307
Hawaii	48.9	0.326	48.0	0.349
Philippines	49.3	0.317	53.5	0.224

The remaining two samples, referred to previously, were known to have been produced in Cuba in the crop year of 1934, on the same plantations from which came two other samples, manufactured in 1935. The analyses made in 1935, of the two pairs of sugars, gave the results shown in Table VI.

TABLE VI. ANALYSES OF TWO PAIRS OF SUGARS

No.	Method I			Method II		
	R	D % R	(S - P)/R	R	D % R	(S - P)/R
70, new crop	0.531	42.4	0.471	0.531	45.6	0.395
69, old crop	1.245	63.1	0.016	1.240	76.5	-0.274
72, new crop	0.431	42.7	0.464	0.430	50.2	0.302
71, old crop	0.991	59.6	0.091	0.985	74.5	-0.234

In both cases the amount of total reducing sugars in the old crop samples is more than twice that in those from the new crop, and at the same time the dextrose ratio is very much higher. Although the sugars were produced in different years, there is a strong indication that the old-crop sugars have undergone inversion during storage, and that levulose has been destroyed through the activity of Torulas. Such cases have also been observed by Browne (2).

The two methods described will next be applied to the analysis of molasses.

Literature Cited

(1) Browne, *J. Am. Chem. Soc.*, **28**, 439 (1906).
(2) Browne, *Louisiana Planter*, **61**, 202 (1918).
(3) Jackson and Mathews, *Bur. Standards J. Research*, **8**, 493 (1932).
(4) Zerban and Wiley, *IND. ENG. CHEM., Anal. Ed.*, **6**, 354 (1934).

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CORRECTION. In the article on "The Determination of Silica in Boiler Water" [*IND. ENG. CHEM., Anal. Ed.*, **6**, 364-7 (1934)] which has been incorporated in the 8th edition of "Standard Methods for the Examination of Water and Sewage," the figure 1.54 given for the dilution factor on page 366 is an experimental one and in the 8th edition has been corrected to the calculated figure 1.56. This figure is independent of any other dilution factor which may enter into the standardization of the color standards used.

M. C. SCHWARTZ

CORRECTION. In the article on "Quantitative Determination of the Concentration of Vaporized Carbon Tetrachloride," by Olsen, Smyth, Ferguson, and Scheffan [*IND. ENG. CHEM., Anal. Ed.*, **8**, 261 (1936)], the first sentence under the heading "Set IV" in the second column should read: "The tests outlined in set II were repeated using the improved method described in set III."

Physical and Chemical Properties of Petroleum Fractions

I. Behavior in Dilute Benzene Solutions

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A modified Beckmann apparatus and method for the cryoscopic determination of molecular weight are described. Results obtained with this apparatus, using benzene as the solvent, are given for oils having molecular weights of approximately 200, 300, 500, and 700.

Comparative cryoscopic data from eleven cooperating laboratories for the same oils in benzene solution are given and discussed.

Data are presented showing that impurities (aside from moisture) and moisture exert adverse effects on molecular weight determinations. The presence of impurities probably at least partly explains the discrepancies universally found in cryoscopic determinations of the molecular weights of oils.

tories cooperated in this work. Most of these laboratories were connected with oil companies, but educational and industrial institutions were also included. A sample of each of the four oils used as solutes, and described below, was sent to each of the laboratories with the request that they determine the molecular weight in their accustomed manner. A questionnaire covering the method, procedure, and solvents used was also enclosed, the data from which are summarized in this report.

Bureau Methods and Apparatus

CRYOSCOPIC METHOD. The cryoscopic apparatus which probably provides the most accurate results is that which employs two cells, as described by Adams (1) and developed further by Kraus and Vinge (13). In this apparatus one cell contains an equilibrium mixture of pure liquid and solid solvent; the other cell contains the solution. Temperature differentials are determined by multiple thermocouples and a potentiometer. The authors' equipment did not permit the use of this more exact method, and the apparatus described below is essentially that of Beckmann, but with several modifications.

Referring to the cryoscopic apparatus, Figure 1, the bath container, *A*, is a double-walled papier-mâché tub such as is used with calorimeters. This is covered at the top by a closely fitting wooden cover, *B*. Through this top, reading from left to right, are the cold-water inlet, *C*, the propeller shaft, *D*, the bath thermometer, *E* (graduated in 0.1°C ., 0.02°C . estimated), the mercury thermoregulator, *F*, the outside jacket, *G*, of the freezing-tube assembly, and the overflow tube, *H*. Referring now to the freezing-tube assembly, the outside jacket, *G*, is 48 mm. in inside diameter and the freezing tube proper, *I*, is 35 mm. in inside diameter. These tubes are held in position relative to each other by a flanged wooden ring, *J*. A close-fitting Bakelite plug, *K*, closes the top of the tube, *I*, and through this plug pass the brass propeller shaft, *L*, and the Beckmann thermometer, *M*.

The propeller proper, *N*, is made from a circular brass disk 19 mm. in diameter, with four radial slots at 90° to each other. The leaves or blades thus formed are slightly tilted out of horizontal to produce pitch. This propeller runs at a speed of approximately 900 r. p. m. To decrease heat conduction from the exterior to the solution, the metal shaft is made in two pieces joined by a glass tube, *O*, and cemented with kaolin and water glass. There is a small air space separating the ends of the shaft within the glass tube. The shaft is mounted in hardwood bearings (not shown), one at each end of the Bakelite plug. Between these bearings the plug is hollowed slightly to accommodate a few strands of oil-saturated cotton, which maintains a film of oil on the shaft without danger of the oil flooding the lower bearing and dropping into the solution below. The Bakelite plug also has a 3-mm. hole (not shown) for the introduction of pellets of solid solutes and for "seeding."

Auxiliary apparatus not shown are an insulated tank for ice water with a magnetically operated valve activated through a relay by the mercury thermoregulator; magnifying glasses for reading the Beckmann and bath thermometers; and a seeding rod consisting of a long glass rod with a 3-strand (No. 30 B & S) nichrome wire coil sealed into one end. The solute, if solid, is compressed into pellets in a stainless steel press; if liquid, it is weighed and delivered from a Nicol tube with the delivery tip bent down. These tubes are filled by suction and the liquid is forced out by air pressure from a small aspirator bulb. The Bakelite plug must be removed momentarily for introduction of liquid solutes.

PRESENT studies dealing with petroleum chemistry now being carried out by the Petroleum Division of the Bureau of Mines included the determination, under comparable conditions, of physical and chemical properties of narrow-cut fractions from selected typical crude oils, coupled with the study of the relationship of these properties to each other, and where possible to similar properties of known compounds. One property that is of importance not only in itself but because of its relation to other properties is molecular weight. This is usually evaluated with data obtained from dilute solutions of the oil in certain solvents. The investigation of dilute solutions of hydrocarbons is interesting from the research standpoint because of the occurrence of many deviations from the theoretical. It seems possible that after suitable study relationships may be found between these deviations and structural differences in the oils and also among certain of the more common characteristic properties, thus giving results of practical value.

Considerable work dealing with the cryoscopic determination of molecular weights has been reported in the literature. Normann (16), in 1907, obtained some interesting molecular weight-concentration curves. Since then Wilson and Wylde (20), Devine (4), Steed (19), Gullick (11), Epperson and Dunlap (6), Fenske et al. (7), and FitzSimons and Thiele (9) have contributed to various phases of the problem. However, each investigator has assumed that his method is correct and has made little attempt to determine why his results do not agree with others. Further, in many cases the oils investigated have not been identified sufficiently to render the data of further use.

The present paper deals with attempts to obtain concordant molecular weights from cryoscopic measurements in dilute solutions of benzene and reports results obtained by the bureau and by cooperative investigators. Sixteen labora-

The pure solvent is placed in the freezing tube, *I*, and weighed quickly to 1 mg., the Bakelite plug with thermometer and stirrer is inserted, and the solvent is cooled until crystallization occurs. It is then warmed slightly, and, in order to obtain constant freezing points, the freezing is repeated three to six times. The solvent is then supercooled without crystallization and placed in the tube, *G*, and stirring begun. Temperature readings are taken at intervals. Since the solvent is below the convergence temperature, it will warm to this temperature and remain constant. For certain solvents, such as cyclohexane, it is necessary to approach the convergence temperature from above as the solvent will not supercool sufficiently without "spontaneous" crystallization. If the convergence temperature thus found is more than 0.1° C. below the freezing point of the solvent, the bath temperature must be increased accordingly.

After the bath temperature is thus regulated the solvent is allowed to cool to the convergence temperature again and is seeded by introducing a small crystal of solvent. Crystallization starts immediately and the temperature rises abruptly to the freezing point, where it remains constant for some time, the length of the plateau varying with different solvents. This freezing point is checked by again warming, supercooling, and freezing. No solute is added until this point will give two consecutive checks within 0.001° to 0.002° C. After this point has been determined accurately a weighed amount of solute is introduced. If the approximate freezing point cannot be calculated, a preliminary freezing of the solution must be made so that proper adjustment of the bath temperature can be made. The process described for the pure solvent is now repeated, except that checks usually are not made, since it has been found that if the first addition of solute is not made until the pure solvent gives check results the freezing points of the solutions generally will check. Three or more additions of solute are made. In certain runs approximately 4 grams of anhydrous magnesium perchlorate were added directly to the solvent in the freezing tube prior to use.

The bureau's cryoscopic apparatus and procedure were developed primarily for research, and the procedure at least cannot be recommended for routine determinations of molecular weight. The experiments have certainly been carried out with more attention to details than is usually expected in a routine laboratory determination.

CALCULATIONS. Both molecular weights and constants for individual determinations have been calculated from the usual relationship between change in freezing point and concentration

$$\Delta = \frac{w}{m} \cdot \frac{M}{W} \cdot K \tag{1}$$

- where
- Δ = depression of freezing point
 - w = weight of solute
 - m = molecular weight of solute
 - W = weight of solvent
 - M = molecular weight of solvent
 - K = molar cryoscopic constant

The concentration of the solute in the solvent has been expressed as grams of solute per gram of solvent

$$C = \frac{w}{W}$$

The final accepted values for both constants and molecular weights have been obtained by extrapolation of a straight line through the points to zero concentration. In the case of the constants, this line was determined by the method of least squares. For determining the molecular weight curves the method of averages was used.

Bureau Solvents and Solutes

SOLVENTS. Benzene is the only solvent discussed in this report, but several supplies of benzene having different degrees of purity were prepared and used.

Benzene A-1 was a reagent-quality thiophene-free benzene and was used without any purification.

Benzene A-2 was prepared from commercially pure benzene by treatment with concentrated sulfuric acid, sodium hydroxide, water, calcium chloride, and distillation from sodium.

Benzene A-4 was prepared from the same benzene as A-2. Two approximately equal portions were separated by crystallization and the crystallized portion was treated with sulfuric acid, water, sodium hydroxide, calcium chloride, and finally refluxed and distilled from sodium. The 4.67 to 90.97 per cent portion was collected and divided into approximately equal portions by crystallization, the crystallized portion being retained.

Benzene A-5 is the mother liquor from the first crystallization of A-4.

Benzenes A-2, A-4, and A-5 were each divided into two portions. One portion, termed "wet," was used as prepared; the other portion, termed "dry," was dried with anhydrous magnesium perchlorate. This same drying agent was used in the determination.

Table I records the freezing points and cryoscopic constant-solute concentration relationships for these solvents. The first numerical term on the right of the equation is the cryoscopic constant at infinite dilution, and the second term gives the slope of the constant-concentration curve. The data are plotted in Figure 3. Rejected data are enclosed within a dotted circle.

TABLE I. DATA ON SOLVENTS

Benzene	Freezing Point		Constant-Concentration Equation	
	Dry ° C.	Wet ° C.	Dry	Wet
A-1	...	5.0	...	$K = 64.98 - 0.16 C$
A-2	5.14	5.08	$K = 66.54 - 0.41 C$	$K = 66.99 - 0.39 C$
A-4	5.53	5.48	$K = 65.42 - 0.02 C$	$K = 68.45 - 0.56 C$
A-5	4.94	4.88	$K = 66.82 - 0.66 C$	$K = 67.63 - 0.47 C$

SOLUTES. Tables II and III give the properties of all solutes used. Naphthalene was used as the standardizing substance for determining the constants of the solvents. Oils O-1, O-2, O-3, and O-4 were employed in the coöperative work. In the studies on the effect of impurities in the solvent only oil O-1 was used.

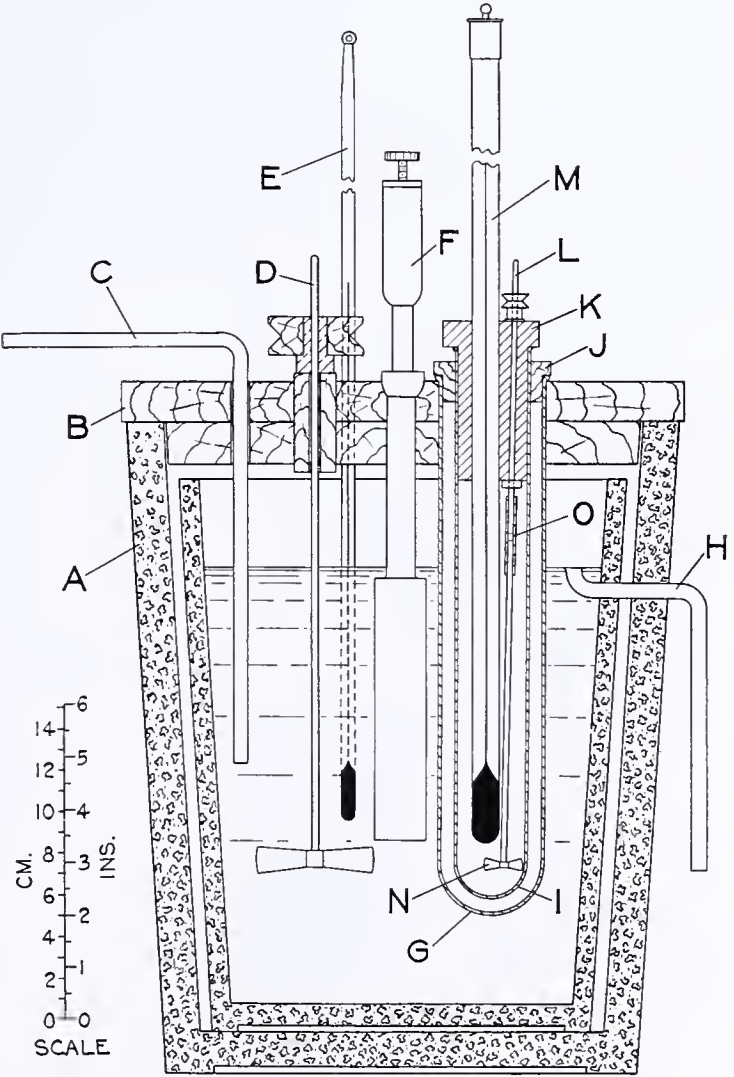


FIGURE 1. CRYOSCOPIC APPARATUS

TABLE II. PROPERTIES OF SOLUTES USED

Number	Name	Source and Purification	Molecular Weight, Theory	Saybolt Universal Viscosity 100° F. 130° F.	Specific Gravity, 60° F.	Approximate Pour Point ° F.	Flash Point ° F.	Carbon Residue %
1	Naphthalene	Pure: treated melted Na; vacuum distilled through Ni on pumice	128.1
2	Triphenylmethane	Pure: twice recrystallized from absolute alcohol, dried at 70° C. under reduced pressure	244.13
3	β -Methyl naphthalene	Practical	142.08
4	Oil O-1	Acetone extract, cuts 91, 92, and 93 Cabin Creek lubrication stock (<i>18</i>) heated in vacuum, filtered hot	1347	550	0.879	30	550
5	Oil O-2	Same as 4, except cuts 61 and 62	259	131	0.863	45	420
6	Oil O-3	Commercial spindle oil	105.4	65.6	0.882
7	Oil O-4	Tops from Port Neches crude by gas distillation at 10 mm. pressure and 156° C. (<i>17</i>), fractionated 40 mm. pressure	40	...	0.888

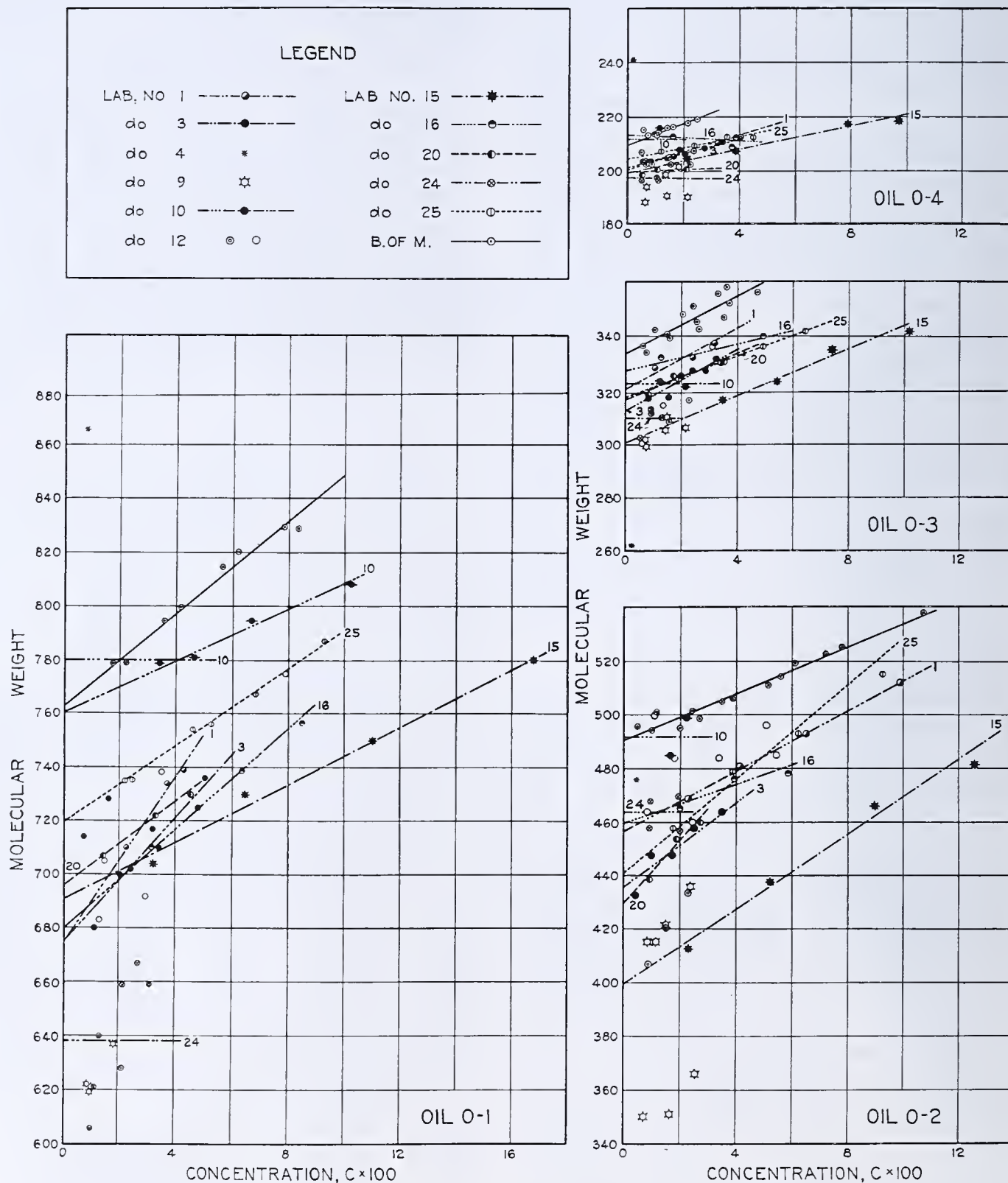


FIGURE 2. MOLECULAR WEIGHT-CONCENTRATION DATA

TABLE III. A. S. T. M. DISTILLATION OF SOLUTE O-4

Per Cent Over	Temperature ° C.
F. D.	464
10	478
20	484
30	487
40	495
50	498
60	504
70	509
80	516
90	527
E. P.	534

ACCURACY. Table IV gives an indication of the accuracy that may be expected from the apparatus described above. In most instances the deviation of the data from the best curve through the data points is of the order of 1 per cent and is almost always within 2 per cent. While the precision obtained is virtually the same for oils over a wide range of molecular weights, there is no criterion by which the accuracy of the molecular weight determination of such oils may be judged.

Coöperative Solvents, Solutes, and Apparatus

Tables V and VI attempt to outline the more significant information concerning the solvents, solutes (besides oils), and apparatus used by the coöperating laboratories by the cryoscopic and ebullioscopic methods. Table VII shows the number of laboratories that used the two methods and the solvents employed.

TABLE IV. MOLECULAR WEIGHTS OF PURE SUBSTANCES IN BENZENE

Solute	Molecular Weight Experimental	Theoretical	Error %	Solvent
Phenyl ether	171.6	170.1	+0.9	A-1
β-Methyl naphthalene ^a	139.5	142.1	-1.8	A-2
Triphenylmethane	242.6	244.1	-0.6	A-1

^a Not purified.

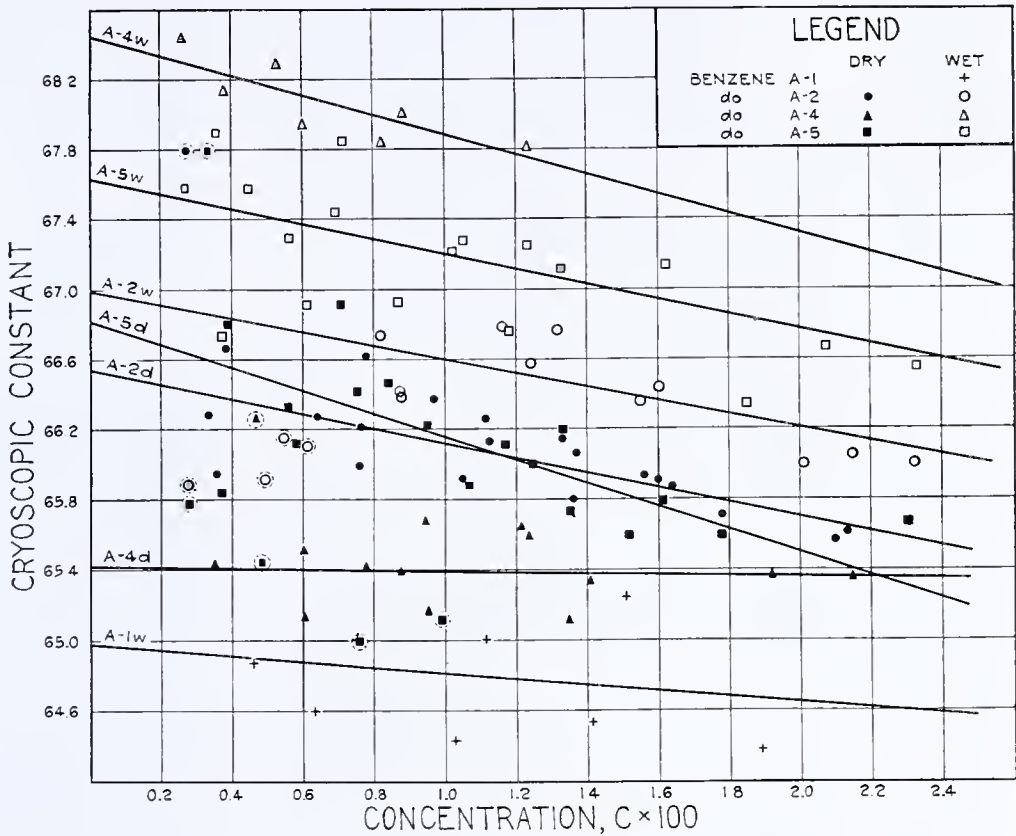


FIGURE 3. CRYOSCOPIC CONSTANT-CONCENTRATION DATA FOR SEVERAL DIFFERENT BENZENES

Benzene is favored in the cryoscopic method. All those laboratories using the cryoscopic method separated the freezing solution from the bath by an air jacket similar to that shown in Figure 1. One laboratory reported using for this purpose a Dewar flask from which the vacuum had been released. A bath temperature of approximately 0° C., maintained by the addition of ice to water, seemed to be the favorite with half of the laboratories reporting; none employed a bath temperature higher than 3.0° to 3.5° C. Stirring of the solution was done universally by means of a wire or glass loop moved up and down in the solution either by hand or mechanically. The replies were not always definite

TABLE V. COÖPERATIVE DATA ON SOLVENTS AND SOLUTES

Lab. No.	Name	Grade	Purified	Solvent		Cryoscopic Constant Molar	Cryoscopic Constant Source	Amount Determined by	Solute Introduced by
				Boiling point ° C.	Ebullioscopic Molar				
1	Benzene	Reagent	No	5.3 ^a	...	65.1	Weight	Dropper
3	Benzene	1° boiling range	Crystallization	69.7	Expt.	Volume ^b	Small pipet
4	Benzene	Unknown	H ₂ SO ₄ , caustic, H ₂ O, dried, fractionated. Thiophene-free	78.5 at 735 mm.	...	59.2	Expt. Azobenzene	Weight	Drops from glass rod
7	Benzene	C. P.	Dried over P ₂ O ₅	80 corrected	33.4 (15)	Volume ^c	Weight pipet
8	Benzene	Industrial pure	Two treatments AlCl ₃	80.1 ± 0.05 corrected	33.4	Volume ^c	Dropper of weighing bottle
9	Benzene	C. P.	No	79-81	...	65.6	(10)	Weight	Dropper
10	Benzene	C. P.	No	79.5-81	...	64.1	Expt. Naphthalene	Volume	Pouring
12	Benzene	Reagent	No	65.6	(8)	Weight	Weight pipet
14	Cyclohexane	C. P.	No	237.9	(5)	Weight	Weight pipet
15	Benzene	C. P.	No	79.5-80.0 corrected	33.4 (3)	62.8	(3)	Weight	Pipet
16	Benzene	C. P.	No	79.5-80	...	65.6	(2)	Weight	Lunge pipet
19	Carbon Tetrachloride	C. P.	No	76-78	34.1	Expt.	Volume	Pycnometer
20	Benzene	C. P.	Fractionation	5.5 ± 0.03 ^a	...	65.6	Heat of fusion data	Weight	Small glass cups
23	Cyclohexane	Reagent	Fractionation	6.1 ± 0.03 ^a	...	243.8	(14)	Weight	Weight pipet
24	Benzene	C. P.	No	240.2	(12)	Weight	Weight pipet
25	Benzene	Reagent	Stored over calcium metal	65.6	Expt. Naphthalene and diphenyl	Volume	Weight pipet

^a Freezing point. ^b Density (12). ^c Density 0.8149 (15).

TABLE VI. COÖPERATIVE DATA ON CRYOSCOPIC METHOD

Laboratory No.	Shield	Freezing Tube Type	Stirrer Speed ^a	Thermometer Tapped	Freezing Bath Material	How stirred	Approx. Temp. °C.	Temp. Diff. Bath and Tube °C.	Freezing Point Checks at Start	Supercooling °C.	Remarks
1	6.3-mm. air jacket	Wire	120	Yes, twice per second	Ice and water	Not stirred	0	5.4	Yes	Freezing tube kept almost airtight except for short time while oil is being added.
3	Air jacket	Stainless steel wire loop	100	Yes	Ice and water	Not stirred	0	5.44	Yes	Freezing tube has ground-glass cover through which thermometer and solenoid stirrer pass, both cemented to the glass. A third opening is provided with ground-glass stopper. Solenoid activated by windshield-wiper circuit breaker. CaCl ₂ added to solvent.
4	1-cm. air jacket	Glass, manually operated		Yes	Ice and water	Manually	0	ca. 5	Before and after determinations	
9	7.9-mm. air jacket	Glass	30	Yes	Ice and water	By electric motor	3.0-3.5	2.0-2.5	Yes	0.3	Cotton placed around stirrer to prevent moisture absorption. Apparatus checked pure substances within 1-3 per cent. Cryoscopic method seems unsatisfactory for oils with weights above 300-350.
10	Air jacket	Wire, cork handle	60	Yes	Ice and water	Metal stirrer manually	2.0	2-3	Yes	0.2-0.3	Temperature of workroom 43° F.
12	Air jacket	Glass	Variable	Yes	Ice and water	Not stirred	0	5.4	Yes	Some runs made with benzene saturated with water.
14	Air jacket			No	Ice and water	Not stirred		2.0	Yes	
15	Air jacket	Wire rod	72	No	Water-ice-CaCl ₂	Manually	-1	6	Yes	Bath temperature controlled by adding CaCl ₂ .
16	Air jacket	Glass, manually operated	120	Yes	Ice and water	Manually	2-3	3	No	
20	19-mm. air jacket	Automatic, nichrome ring	75	Yes	Ice and water	Air bubbles	2-3.5	2.5	Yes	1 to 2 grams of anhydrous.
23	Air jacket	Glass spiral	130	Yes	50% alcohol	Circulating pump	3	ca. 3.5	Yes	Anhydrous sodium sulfate added. To obviate excessive supercooling glass thimble below solvent tube filled with chilled mercury makes contact with platinum wire fused in bottom of solvent tube. Low temperature of wire causes crystals to form on it which are knocked off by stirrer.
24	Dewar flask, vacuum released	Pt rod vertical motion mechanical	36	Yes	Ice and water	Not stirred	0-1	4-5	Yes	Barium perchlorate added.
25	5-mm. air jacket	Reciprocating	120	Yes	Ice and water	Manually	0	5.4	Yes	0.2-0.3	Anhydrous sodium sulfate used. Benzene stored over sodium sulfate. Air jacket filled with water to obtain rapid cooling, then removed for actual determination of freezing point. Necessary to stir solvent for about 10 minutes before constant freezing point values can be obtained.

^a Strokes per minute.

on this subject, but hand stirring seemed to be the rule in two-thirds of the laboratories. The information received pertaining to the degree of supercooling allowed or obtained in the solution before freezing began was rather meager but consistent at around 0.2° to 0.3° C. About half of the laboratories favored a dehydrating agent in the freezing solution, and all measured temperature with a Beckmann thermometer. Only the data reported for the cryoscopic method with benzene are discussed in this report.

Experimental Results

Although the results given in this section are called "molecular weights," attention is called to a discussion of this term below.

COÖPERATIVE DATA. Figure 2 shows all the data obtained by the coöperating laboratories, together with some data by the Bureau of Mines on the determination of the molecular weights of the oils by the cryoscopic method with benzene. Wherever a laboratory has reported an extrapolated value for molecular weight, a line has been drawn through the data points from the extrapolated or "accepted" molecular weight at zero concentration. If the laboratory averaged a series of determinations, this is shown by a straight horizontal

line drawn through the data points from the accepted molecular weight at zero concentration. Where the laboratory has only submitted data with no choice of accepted molecular weight, no attempt was made to determine a molecular weight representing the data, and only the points are shown in the figures. In the case of Laboratory No. 12, two series of determinations were made by the cryoscopic method in benzene; in one series the solvent had absorbed some moisture from the atmosphere and in the second the solvent was saturated with water. Two different symbols are used to indicate this. Bureau data on oils O-1 and O-2 were obtained with solvent A-1 (wet), and on oils O-3 and O-4 with solvent A-2 (wet).

TABLE VII. DISTRIBUTION OF METHODS AND SOLVENTS EMPLOYED BY COÖPERATING LABORATORIES

Solvent	Cryoscopic Method	Ebullioscopic Method
Benzene	11	3
Cyclohexane	3	0
Carbon tetrachloride	0	1

The spread in the molecular weight data for each oil as reported at or near infinite dilution is approximately as follows: oil O-1, 35 per cent; oil O-2, 34 per cent; oil O-3, 24 per cent; oil O-4, 12 per cent. The mean values of the extrapolated or averaged molecular weights, exclusive of the

bureau result are: oil O-1, 693; oil O-2, 447; oil O-3, 317; oil O-4, 204. The comparative bureau results on these oils are 763, 491, 333, and 209, respectively. These figures are higher in every case, and further, almost without exception, the bureau data are higher than the highest reported by the cooperating laboratories. There appear to be three possible causes for this discrepancy: the use by the bureau of a much more effective method of stirring, a bath temperature only slightly below the freezing point, and slightly impure solvents. The last-mentioned possibility will be discussed here.

EFFECT OF SOLVENT IMPURITIES ON CRYOSCOPIC CONSTANT. Figure 3 and Table V present the data obtained for the determination of the cryoscopic constant of the several benzenes studied. Naphthalene from the same lot was used in all the runs. It will be noted that the constant-concentration ($K - C$) curve for the purest solvent, A-4 (dry), has virtually no slope, and the extrapolated value for the constant agrees very closely with the theoretical value of 65.17. When A-4 is used without drying, the value of the constant is increased 4.6 per cent and the slope of the $K - C$ curve increases greatly. The values for A-2 (dry) and A-5 (dry) are very near each other, but both are higher than the value for the pure benzene, A-4 (dry). Without the use of a drying agent, the values for A-2 and A-5 both increase, in A-5 more than A-2, but neither reaches the value of A-4 (wet). The slope of the $K - C$ curves for A-2 and A-5 does not change a great deal, whether the solvent is moist or dry, and is about the same as the slope of the A-4 (wet) curve. The authors interpret the above facts concerning naphthalene in benzene through the concentrations used as follows:

- 1. The $K - C$ curve for pure dry solvent will have almost no slope and by extrapolation will give a value that virtually agrees with the theoretical.
- 2. The presence of impurities (aside from moisture) in the solvent will lead to higher values for the constant and cause considerable slope in the $K - C$ curve.
- 3. The presence of moisture in otherwise pure solvent greatly increases both the value of the constant and the slope of the $K - C$ curve.
- 4. The presence of moisture in impure solvent increases the value of the constant somewhat, but makes little change in the slope of the $K - C$ curve.

In general, concordant check results are not obtained as easily with moist as with dry solvent. Mention should be made of the data for A-2 (wet). The first four points, which show a definite trend down (positive slope), were not used in calculating the constant. There is some justification for this as no other solvent showed this trend and all the other curves have a negative slope, including A-2 (dry). Actually, it probably is erroneous to draw the curve as has been done, but the error involved should be small and make little difference in the subsequent molecular weight determinations. Solvent A-1, which is marked "wet," was used during very hot, dry weather, and it is probable that its moisture content was low. Further, it was originally reagent-grade benzene, thiophene-free.

EFFECT OF SOLVENT IMPURITIES ON MOLECULAR WEIGHT OF OIL O-1. The molecular weight of oil O-1 was determined in each of the benzenes previously described, using the constants determined as above. The results of these determinations are shown in Figure 4 where each curve represents data provided by two to six series of determinations. The values of the molecular weight increase with increase of solute concentration in every solvent, and the rate of increase is very similar for each solvent. The extrapolated values differ in extreme by 13.3 per cent, yet they were obtained with the same oil, the same apparatus and method, and the same operator; and, further, the constant for each benzene was determined identically with naphthalene. Since the average deviation of the experimental values from those calculated by the molecular weight concentration relationship for a series of determinations is only about 1 per cent, the effect of variation in purity of solvent is obvious. An examination of Figure 4 indicates that for solutions of this oil in benzene the following observations hold:

- 1. There is a very definite increase in molecular weight values with increase in concentration of solute.
- 2. The rate of increase tends to be higher with solvents containing impurities, especially moisture, but in general the slope is very similar regardless of degree of solvent purity.
- 3. There is a definite increase in the extrapolated value of the molecular weight with increase of impurities (aside from moisture).
- 4. The presence of moisture decreases the extrapolated value of the molecular weight. This effect is greater in a pure solvent than in an impure one.

Discussion

There seems to be no doubt, in view of the data presented, that impurities (including moisture) have a marked effect on the determination of molecular weights by the cryoscopic method in benzene. It seems probable that other solvents will be affected similarly by impurities.

The discrepancy previously noted, regarding the results obtained in the cooperative work, can be explained, partly at least, by probable variation in solvent impurities and moisture content. The error that can result from using the theoretical constant for the solvent regardless of purity is apparent. Further, the experimentally determined constant does not entirely compensate for the effect of moisture and impurities. The only safe procedure appears to be to use the purest solvent possible and to determine its

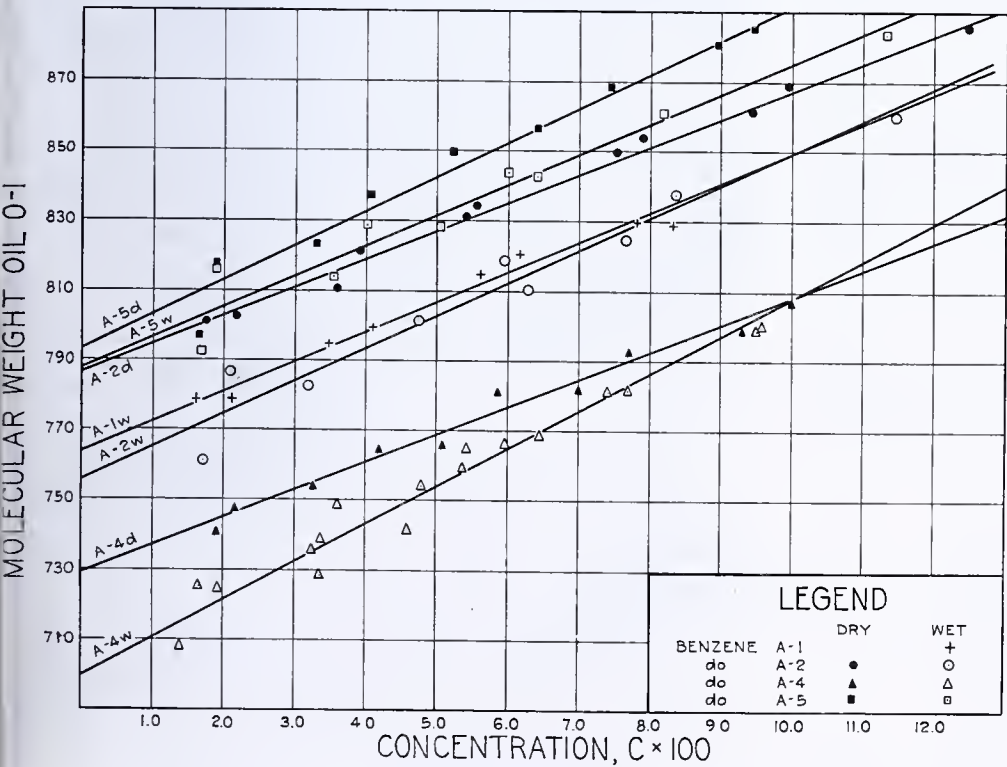


FIGURE 4. MOLECULAR WEIGHT-CONCENTRATION DATA FOR OIL O-1 IN SEVERAL DIFFERENT BENZENES

constant with a known pure solute. In addition, a drying agent should always be used. Anhydrous magnesium perchlorate has been found to be satisfactory for this purpose.

Three possible causes for the high values of the bureau results have been mentioned. Of these, the presence of impurities and moisture in the solvent has been studied. These probably are contributing causes of the high molecular weight values previously noted. The lowest experimental value that could be obtained, with solvent A-4 (wet), is above almost all values reported by the coöperating laboratories. It is obvious that some other factor, presumably either the more effective stirring or the higher bath temperature, or both, is a contributing influence.

The term "association" has been used by many writers to explain the increase in molecular weight with increase in concentrations of solute in solvent. However, the authors have found several cases of what, in the same terminology, should be called "dissociation." Cyclohexane gives results of this type. It is difficult if not impossible to find a satisfactory conception of association or dissociation as applied to non-electrolytes. However, if the slope of the molecular weight-concentration curve is assumed to be the result of abnormal solute characteristics rather than the result of some solvent peculiarities, then oils must be considered as mixtures of molecules of different sizes and kinds existing in some type of molecular aggregation even at infinite dilution. This assumption permits at least of a partial explanation of the concentration effect. From this point of view, although the term "molecular weight" has been used in this paper, it probably has little meaning as such. Rather, a variable is determined which is called "molecular weight" and which represents the state of molecular aggregation of the oil in the solvent at the concentration in effect at the time. Generally it is found that in dilute solution the value of this "molecular aggregate" changes uniformly with changes in concentration, and a value at infinite dilution may be obtained by extrapolation. This is the value of the molecular aggregate at infinite dilution in a given solvent, and might be termed the "apparent molecular weight in benzene, cyclohexane, etc." Under ideal conditions such extrapolated points may coincide for the solvents under investigation, and this point may be called the most probable "molecular aggregate at infinite dilution." Whether the entire explanation of the slope of the molecular weight-concentration curve can justly be placed upon association or dissociation of the solute appears uncertain and remains for further research. It is hoped that the manner in which different oils behave in the same and different solvents will furnish information as to their possible type, methods of separation, and relation to other physical and chemical characteristics.

Acknowledgment

The authors wish to express their appreciation to the laboratories who coöperated with them by providing data used in this report and for their suggestions and criticisms.

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Nesslerization Applied Directly to a Macro-Kjeldahl Nitrogen Determination

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IN STUDYING the nitrogen content of tissues the authors were confronted with the need of finding a simple procedure for accurately weighing small samples of wet material. They found that samples of ground fresh material, containing about 15 mg. of nitrogen, can best be weighed on tin foil.

The sample is placed on a weighed piece of foil, which is quickly folded in such a way as to prevent any loss of moisture, and weighed. The weight of the sample is determined by difference. The wrapped material is dropped into a Kjeldahl flask containing 5 cc. of concentrated sulfuric acid, without possibility of loss at any stage of the operation. The digestion is carried out as usual with the aid of a few drops of superoxol. The tin foil serves also as a catalyst and the digestion proceeds rapidly to completion.

A further simplification of the procedure consists in the substitution of direct nesslerization for the usual distillation. The clear, colorless digestion mixture is transferred quantitatively to a 250-cc. volumetric flask and diluted with water to the mark. The tin is precipitated upon dilution and may be either centrifuged off or allowed to settle out spontaneously. An aliquot of the clear solution, corresponding to 0.7 to 1.5 mg. of nitrogen, is measured into a 100-cc. volumetric flask, while a standard containing an appropriate amount of nitrogen (usually 1.0 mg.) and a similar concentration of sulfuric acid is prepared in another flask. The contents are diluted to about 60 cc. with distilled water, Nessler solution is added (30 cc. for 1 cc. of sulfuric acid) and made up to volume. The colors are matched in a colorimeter as usual.

The authors have checked the accuracy of this procedure by comparing the results of the direct nesslerization with the distillation results, also by analyzing the nitrogen content of pure compounds (urea), and have found this procedure absolutely reliable. Although their primary objective was to devise a way of handling wet tissue, the method for nitrogen determination as here outlined has wider application and can be used successfully whenever it is desired to eliminate the distillation. The authors used selenized granules as catalyst in some digestions and found that the direct nesslerization could also be employed here.

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Organic Microanalysis

I. Nitrogen by Dumas Method

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DURING the last four years over a thousand organic compounds have been analyzed in this laboratory. These compounds have been of the most varied types, and the original methods of Pregl (10) as well as many modifications suggested later have been checked carefully. A brief description of the apparatus and procedure now employed should be of assistance

to all microanalysts. The analysis is easier, quicker, and somewhat more accurate than when using Pregl's directions.

Carbon dioxide generators of the Kipp type, using the procedure recommended by Pregl, were found unsatisfactory because of the short life after the exhaustive purification required. Various modifications with provision for the use of carbon dioxide above the acid (3, 5, 13) were tried and discarded because they were cumbersome or difficult to manipulate. Generators using a solid carbonate with heating were unsatisfactory because of the troublesome heating required before use (4, 8). The generator described by Poth (9) in its original form (no advantages were found for the modified generator, 7) has proved the best. Such generators after careful filling deliver to a small mercury-filled gasometer carbon dioxide which contains less than 0.001 per cent impurity (not condensed by liquid air). One filling will deliver about 100 liters of carbon dioxide and the gas is uniformly pure and available on turning a stopcock.

The most careful recent study of the Dumas method has been made by Trautz (12), and the combustion tube filling and the combustion procedure follow his directions. The points discussed below, however, differ from Trautz.

Apparatus

An electric furnace, split type, was constructed cheaply by boring a 1.1-cm. (0.44-inch) hole lengthwise through an Armstrong refractory brick, cutting the brick in halves, and then cutting eight slots around the periphery of this central hole with a hacksaw blade. Nichrome wire, No. 26, was laid in these slots, hair-pin fashion, and held in place by a light coating of alundum cement. The two halves were mounted in sheet-metal holders hinged together and held on a rod. Such a furnace, with the two halves connected in series, has a resistance of about 10 ohms and, when carrying a current of approximately 4 amperes regulated by a General Radio Co. Variac, is easily maintained at 700° C. A thermocouple buried in the alundum lining indicates the temperature on a calibrated millivoltmeter.

The replacement of the long burner with this electric furnace has proved very advantageous. The furnace can be opened, slid back, and the tube cooled with an air blast in 10 minutes, so that there is no time lost before the next analysis. Likewise the heating of the room is greatly reduced. The tube now in use, of Jena

An all-glass apparatus, which is easily handled and includes an improved azotometer without stopcock, has been designed and used in many hundred analyses. All arbitrary procedure in correcting for errors has been eliminated and the corrections have been experimentally determined. More accurate results are thus obtained without excessive time or attention.

Supremax glass, has been used for several hundred analyses with no sign of deterioration; in fact, mechanical fracture has been responsible for the loss of all tubes since using the electric furnace.

The movable Bunsen burner is equipped with a wing tip and mounted on a heavy base plate by a rough rack and pinion, paralleled by a scale ruled on the base. This enables the burning to be accomplished very smoothly and regularly. The burner is advanced 1 cm. per minute until decomposition

starts and, after that, 1 or 2 mm. per minute until the desired bubble rate is reached. Since the burner is never advanced too far by a slip of the hand, very little attention is required for the combustion. With the azotometer now in use, the analysis is finished 25 minutes after the end of the first burning. On the average 1.25 hours are required for an analysis, allowing 30 minutes for the first combustion.

The azotometer is made of Pyrex glass designed without a stopcock at the top. Difficulty was always experienced with the stopcock of the old type of azotometer. Either grease would contaminate the potassium hydroxide or the stopcock would freeze on standing idle for short intervals. The present azotometer has a cup opening at the top, closed by a short glass rod ground into the azotometer tube. There is no constriction of the graduated portion of the tube, such as there was in the old azotometer. Smaller volumes of nitrogen can be read and the use of a trace of ceresin on the ground joint has eliminated sticking. The plug is sealed by the alkali itself and can be held firmly seated by a rubber band stretched over it. The graduated portion with ground-in plug can be made at moderate cost by any apparatus maker and, after calibrating with mercury, can be seated to the wide lower portion of the azotometer. Pyrex resists the action of alkali very well, since recalibration after one year's use showed no deviation greater than 0.001 cc. from the original Bureau of Standards calibration. The potassium hydroxide solution is made of equal weights of c. p. stick potassium hydroxide and distilled water without any additional treatment. The potassium hydroxide is renewed after approximately ten analyses and sticking of bubbles at the mercury surface is rarely encountered.

The size of the opening through which the bubbles enter the azotometer is of importance, but cannot be regulated easily, since in sealing on the capillary inlet tube (approximately 0.8 mm. inside diameter) it is impossible to avoid widening it slightly. The volume of one bubble can, however, be easily ascertained. In the azotometer now in use 1 bubble equals 0.0167 cc. Weygand (13), who discusses this point at

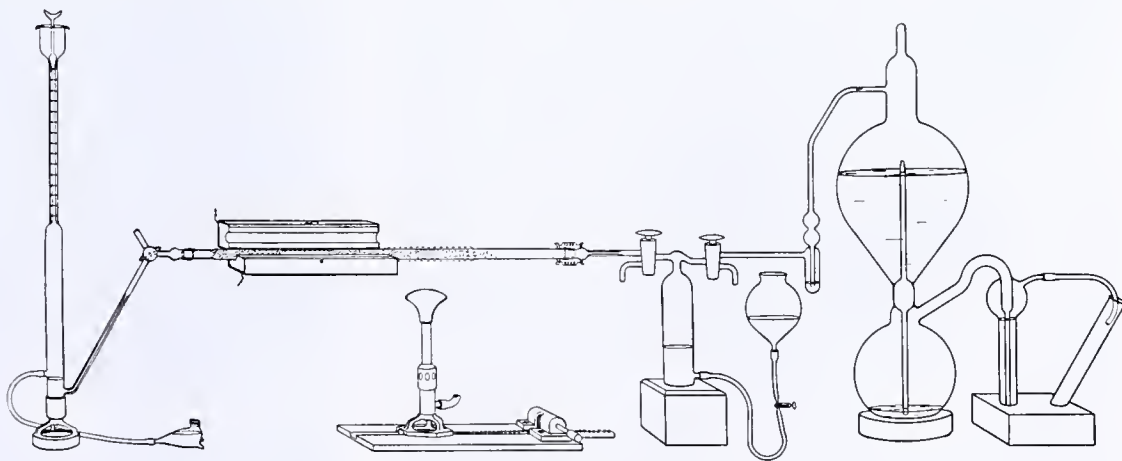


FIGURE 1. DIAGRAM OF APPARATUS

some length, has an obvious misprint (p. 29) in giving the volume of 20 bubbles as 4.0 cu. mm. or less. Friedrich probably gives the best criterion for true microbubbles—namely, their uncertain, slow (40 to 90 seconds) rise in the graduated part of the azotometer. Naturally, each azotometer is different with respect to the volume of the single bubbles so that the rate of burning employed and the size of the final microbubbles will vary, depending on the diameter of the azotometer inlet tube.

The gas collected in the azotometer is subject to three corrections: (1) the wall error of the azotometer, (2) the vapor pressure of the alkali solution, and (3) the nitrogen present in the carbon dioxide or in the interstices of the tube filling or leaking in through the rubber connections. All the above corrections were considered by Pregl to be satisfactorily taken into account by the deduction of 2 per cent of the gas volume as read. Of this, 1.5 per cent was supposedly due to the wetting of the walls and 0.5 per cent was due to the vapor pressure of the potassium hydroxide solution. Trautz later pointed out after careful experiments that the wall error was really only 0.5 per cent. This has been confirmed by measurements made in this laboratory.

Trautz also assumed (p. 308) that the vapor pressure correction was only 0.3 per cent. However, measurements made by Clark (1) as well as some made in this laboratory show this to be too low. The method of Smith and Menzies (11) was used and both fresh and used (10 analyses) potassium hydroxide solutions were measured. The results are shown in Table I. For comparison the values found by Clark and data interpolated from International Critical Tables (6) are given. The agreement among the results is not very good, but it is sufficient for the purposes of the correction, and the values from International Critical Tables have been used as the best basis for the correction. As can be seen, the variation with temperature is such that no simple correction for all temperatures can be made. Accordingly the values from the International Critical Tables have been used to construct a table of corrections to be applied to the barometric reading.

TABLE I. VAPOR PRESSURE OF POTASSIUM HYDROXIDE

(Vapor pressure, in mm. of mercury, of solution containing approximately 71.5 grams of potassium hydroxide per 100 grams of water)

Temperature ° C.	Fresh Solution	Used Solution	Clark	I. C. T.
15	2.9	3.5	5.5	4.1
20	4.3	5.1	7.0	5.6
25	6.1	7.1	8.9	7.4
30	8.4	9.6	11.4	9.6
35	11.4	12.9	14.0	12.7

The value of the last correction, for air leakage or adsorption, depends on both the manner in which the apparatus is assembled and the pressure relationships within the combustion tube. Using the azotometer in its holder, as usually purchased, with the combustion tube about 22.5 cm. (9 inches) above the desk top it is found that, even with the alkali leveling bulb lying on the desk top, a pressure greater than atmospheric exists within the combustion tube. With rubber connections in the train, this may well lead to low nitrogen values. If, however, a 0.5 or 0.3 per cent correction has been made instead of the true, higher correction for vapor pressure, this error may be compensated and approximately correct nitrogen values found. Unless the rubber is exceptionally tight, it is almost impossible to guard against leaks either into or out of the tube because, during a combustion, the pressure within the tube will vary appreciably as the gas collects in the azotometer.

The all-glass apparatus now in use in this laboratory has a combustion tube with two ground-glass joints with the final stopcock sealed directly to the azotometer. Since all regulation of the gas flow is accomplished by the cock on the carbon

dioxide gasometer, this final cock is a three-way one, so that the tube can be evacuated before starting the combustion. In this way the measured error due to air in the carbon dioxide and adsorbed on the copper oxide has been reduced to 0.002 cc. On compounds of known purity, values are consistently obtained within less than ± 0.1 per cent of theory.

TABLE II. NITROGEN CONTENT OF SOME REPRESENTATIVE COMPOUNDS

	Found, Dumas	Calculated	Found, Kjeldahl
Azobenzene, $C_{12}H_{10}N_2$	15.44	15.39	...
Ammonium sulfate, $(NH_4)_2SO_4$	21.10	21.20	...
Urea, CH_4ON_2	46.61	46.66	...
1,2-Dihydro-2-keto-4-ethoxypyrimidine, $C_8H_9O_2N_2$	20.11	20.01	...
Parabanic acid, $C_5H_5O_3N_2$	24.56	24.57	...
6-Methyluracil, $C_6H_5O_2N_2$	22.22	22.22	...
1-Tetraacetylglucosido-7-acetylcytosine, $C_{20}H_{25}O_{11}N_3$	8.86	8.70	...
1-Glucosidocytosine nitrate monohydrate, $C_{10}H_{15}O_6N_3 \cdot HNO_3 \cdot H_2O$	15.59	15.82	...
1,2-Dihydro-2-keto-1-ethyl-4-ethoxy- pyrimidine, $C_9H_{12}O_2N_2$	16.47	16.66	16.71
	16.39		16.77
Cytosine, $C_4H_5ON_3$	32.13	37.84	37.58
	35.05		37.63
1-Methylcytosine, $C_5H_7ON_3$	31.72	33.60	33.58
	32.52		33.63
5-Bromouracil, $C_4H_3O_2N_2Br$	14.04	14.67	14.55
	14.17		14.70
2,4-Dimethoxy-5-bromopyrimidine, $C_6H_7O_2N_2Br$	10.71	12.79	12.89
	11.33		13.02

Some years ago it was found that, contrary to the statements in many standard texts, some compounds cannot be analyzed correctly by this method even when potassium chlorate is used. This has recently been pointed out by Friedrich (3, p. 74). The last half of Table II gives some examples that have been found in this laboratory. The Kjeldahl method used, which does not involve any preliminary reduction or treatment, will be described in a forthcoming note.

No generalizations can be made because, while bromine appears to be a disturbing factor, it is not present in the cytosines which also give low values. Likewise, in this apparatus, compounds such as urea, containing a high percentage of nitrogen, are analyzed with success. In the analysis of pyrimidines and possibly other cyclic ureides, imidazoles, and purines which are often obtained from natural products, it would seem best to check the Dumas nitrogen values by the Kjeldahl method. Many compounds have been encountered which stick so obstinately to the sides of the mixing tube, especially in winter when the relative humidity is low, that now, as a matter of routine, all weighings are made in porcelain boats and mixed with fine copper oxide after introduction into the combustion tube. This has also been experienced by others (2).

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Apparent and True Solids of Sugar-Cane Juice

Relation of Difference to Ash Content

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IT IS OBVIOUSLY proper to append the conditional term "apparent" to the per cent solids or degree Brix of impure sugar solutions when they are determined by any specific gravity method, because such an estimation is partly based on the false premise that the various impurities have the same specific gravity as sucrose. It is generally known that the apparent solids of cane juice, sugar-house sirups, and molasses are considerably higher than the actual solids found by drying. The principal cause of this difference between apparent and true solids is the effect of the high specific gravity of the salts present in these products as compared with the density of sucrose itself. The influence of the reducing sugars and the organic nonsugars is thought to be of small importance and probably tends to counteract slightly the effect of the inorganic constituents. Discussion of these points will be found in the handbooks by Browne (3) and Spencer and Meade (9) and in papers by Hill (6) and King (7).

Little information has been found in the literature concerning the amount of the difference between apparent and true solids or of its mathematical correlation with the ash content except that given by King (7) for Philippine molasses. King published a summary of the observed differences between the apparent and true solids of a large number of molasses samples and showed that there existed a general relationship between the amounts of these differences and the ash contents. He proposed the calculation of the true solids from the apparent solids and ash by use of an ash factor. In view of his results, the data on solids and ash of some crusher juices which were analyzed during a general study of juice composition in Louisiana have been examined, and the results of this work form the material for the present discussion.

Experimental

During the 1931 cane harvest over 200 samples of crusher juices representing various cane varieties, soil types, and fertilization tests were obtained through the coöperation of the Divisions of Sugar Plant Investigations and Soil Fertility Investigations of the Bureau of Plant Industry, stationed at Houma, La. These raw juices were first freed from such adventitious coarse suspended material as could be removed by a standardized moderate centrifuging in a solid basket, followed by screening through a 200-mesh sieve. The apparent and true solids and the ash were then determined.

The apparent solids or apparent ° Brix were estimated with a Brix spindle calibrated for 17.5° C., and the observed reading was corrected to that temperature by the usual tables. Solids by drying were determined by the official method of the Association of Official Agricultural Chemists (2), the drying being completed in a constant-temperature vacuum oven operated at 70° C. and a vacuum of 27 inches. Numerous duplicate tests made to determine the degree of precision of the methods indicated that for the apparent solids the average deviation from the mean was probably $\pm 0.05^\circ$ Brix or more, whereas for the solids by drying the deviation was only ± 0.01 per cent solids.

The ash content was determined by evaporation of a definite quantity of juice to a thick sirup over a water bath, followed by gentle charring over a hot plate. The ignition was completed in an electric muffle at not over 500° C. Ash content was calculated as percentage based on apparent solids. For duplicates the average deviation from the average was ± 0.03 per cent ash.

In addition to these tests on raw juices about 4 liters (1 gallon) of each lot of juice were clarified by a standard method, using either lime alone or the sulfur-lime process. The clarified juices were evaporated to about 55° Brix in a vacuum pan. The

sirups were subsequently diluted to approximate juice density and analyzed in the same manner as the raw juice.

Discussion of Results

The observed differences between apparent and true solids ranged from 0.21 to 1.24. The frequency curves in Figure 1 summarize the complete data on the amounts of these differences and also on the percentages of ash. These curves, although they do not take into account the concentration of total solids, do exhibit a general relationship to each other. The differences between apparent and true solids are much larger than the combined experimental errors, and hence it follows that they are due principally to the intrinsic composition of the juices and must be related to the quantity or the specific gravity of the nonsugar constituents, or both.

The experimental errors, particularly in the apparent solids determination, affect considerably the differences between the apparent and true solids found in individual determinations. For the same reason any correlation of ash with these differences, when considering samples singly, may give erratic results concealing the probable relationships. However, since the errors involved are random, rather than systematic, it follows that the average of the results from a number of tests will be more reliable and the correlations will be more evident.

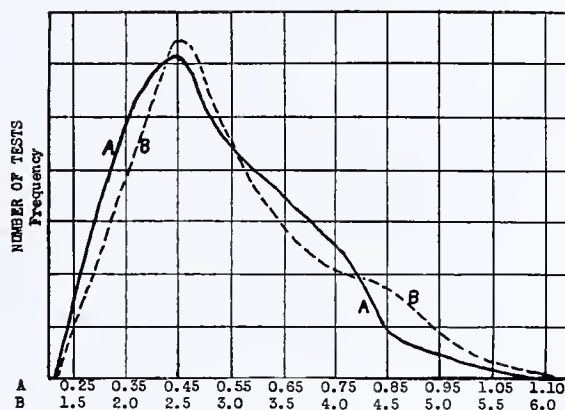


FIGURE 1. FREQUENCY CURVES

- A. Difference between apparent and true solids
B. Per cent ash, based on apparent solids

The data were therefore grouped and averaged, first by cane variety, using only such tests as were strictly comparable. It was found that the average difference between the apparent and true solids was different for each of the six varieties compared and was related to the characteristic ash content of the variety. In like manner, other data were grouped and averaged according to soil type and also with respect to fertilizer treatment, and were found to give average differences between apparent and true solids which were definitely related to the ash content of the juices. A general correlation was apparent, and it remained to determine the mathematical expression.

It is probable that two principal factors influence the magnitude of this difference between the apparent and true solids: first, the ratio of the ash to the total solids, and, second, the concentration of the solids. The former determines the deviation of the specific gravity effect of the solids from that of pure sucrose produced by the ash, and the latter is concerned with

TABLE I. DIFFERENCE BETWEEN APPARENT AND TRUE SOLIDS AND CORRELATION WITH ASH CONTENT OF INDIVIDUAL SAMPLES OF CRUSHER JUICE

Sample	A Apparent Solids %	B True Solids %	C Difference, A - B	D Ash based on Appar- ent Solids %	X Quotient, C/D	Final Factor, X/A
1	16.09	15.70	0.39	1.95	0.200	0.0124
2	15.26	14.77	0.49	3.09	0.159	0.0104
3	15.36	14.77	0.59	3.43	0.172	0.0112
4	14.76	14.08	0.68	3.49	0.195	0.0132
5	14.21	13.44	0.77	4.56	0.169	0.0119
6	14.46	13.59	0.87	4.73	0.184	0.0127
7	12.19	11.47	0.72	4.63	0.155	0.0127
8	14.01	13.37	0.64	3.69	0.173	0.0123
9	15.11	14.61	0.50	2.46	0.203	0.0134
10	16.64	16.06	0.58	3.44	0.169	0.0102
Average					0.178	0.0120
Average deviation from average					±0.014	±0.0010

TABLE II. DIFFERENCES BETWEEN APPARENT AND TRUE SOLIDS AND CORRELATION WITH ASH CONTENT

(Based on averages for seven crusher juice samples for each sugar-cane variety)

Sugar-Cane Variety	A Average Apparent Solids %	B Average True Solids %	C Average Difference, A - B	D Average Ash Based on Ap- parent Solids %	X Average ^a Quotient, C/D	Average ^a Final Factor, X/A
POJ 36M	14.99	14.50	0.49	2.80	0.178	0.0119
POJ 213	14.58	14.03	0.55	3.01	0.186	0.0128
POJ 234	15.52	14.97	0.55	3.13	0.181	0.0117
Co 281	15.65	14.96	0.69	3.63	0.191	0.0122
Co 290	15.25	14.56	0.69	3.73	0.191	0.0125
CP 807	14.52	13.89	0.63	3.44	0.185	0.0127
Average			0.60	3.29	0.185	0.0123
Average deviation from average			±0.07	±0.31	±0.004	±0.0004
Significant differences: ^b						
P = 0.05			±0.05	±0.17	±0.018	±0.0013
P = 0.01			±0.07	±0.23	±0.024	±0.0017

^a Averages of quotients calculated for individual data.^b The statistical differences were calculated by using the formulas of Fisher (4) to correct for correlated variations. The application of these formulas to field tests on sugar cane has been made by Arceneaux (1).

the total effect on the weight of a particular quantity of solids of this density. Although the composition of the ash, and consequently the specific density effect of the salts, is somewhat variable, there is no evidence that this variation is sufficient to alter significantly the average specific gravity of the total inorganic material.

Based on this reasoning a factor was derived as follows: (1) the observed difference between apparent and true solids was divided by the percentage of ash (based on apparent solids content) and (2) this quotient was divided by the percentage of apparent solids. The first quotient gives the difference between apparent and true solids due to 1 per cent of ash, and the factor in its final form expresses the difference for each 1 per cent of solids due to each per cent of ash.

It is impractical to include all the data in this publication, but two tables are presented as examples of the method outlined and of the results obtained. Table I shows the data for a representative group of samples selected to give a typical cross section of all the juices tested. The average variation in the derived factors is equivalent to only ±0.05 per cent solids, which is essentially the experimental error of the apparent solids determination. Table II gives the averages of groups of seven tests for each of six commercially important cane varieties, and shows the increased uniformity in the calculated factors which is attained by dealing with averages instead of single determinations. The group factors have a much smaller deviation from the general average than those of individual tests.

Statistical examination of the data presented in Table II shows that in the actual amounts of the differences between the apparent and true solids there are several comparisons which indicate highly significant differences between certain varieties. These of course correspond to significant differences in

the ash contents. For the correlative factors that were derived, however, even the maximum variation between the varieties is much less than the value required to be moderately significant. This indicates that, in the average factors, for all practical purposes one is dealing with a constant. Similar studies of the results from samples, comparing the effect of soil type and of fertilizer treatment, likewise show that these conditions affect the apparent and true solids, their difference, and the ash content of the juice, but do not significantly change the value of the derived correlative factor.

The general average of all the factors calculated from these analyses of crusher juices from Louisiana sugar cane was found to be 0.0120, and the average factor for the corresponding sirup samples was 0.0108. This lower value of the factor for sirups is possibly due to the elimination of the phosphate ions during clarification.

An example will illustrate the use of these factors in estimating the true solids from the observed apparent solids and ash. Assume a raw juice of 17.0° Brix with an ash content of 2.5 per cent on solids. To find the probable difference between the apparent and true solids, multiply as follows: 0.0120 × 17.0 × 2.5, which yields the value 0.51. Subtracting this amount from the observed apparent solids, one obtains 16.49 as the estimated true solids.

The use of the factors may be simplified by the construction of a suitable nomograph or table for the range of ash and solids commonly encountered. Figure 2 and Table III exemplify such arrangements applied to Louisiana crusher juices. In presenting these factors and the table for converting apparent to true solids, it is not claimed that these particular values will hold universally. Differences in the technic of the determinations of the apparent and true solids and the ash will cause variation in the factors from the values given; also, differences in ash composition will produce slight changes in the factors. Nevertheless the values given may be very close to those that would be obtained from a much greater number of tests and from other locations, for the samples included in this study represented a wide variation in both per cent of ash and ash composition. The cane used was grown on

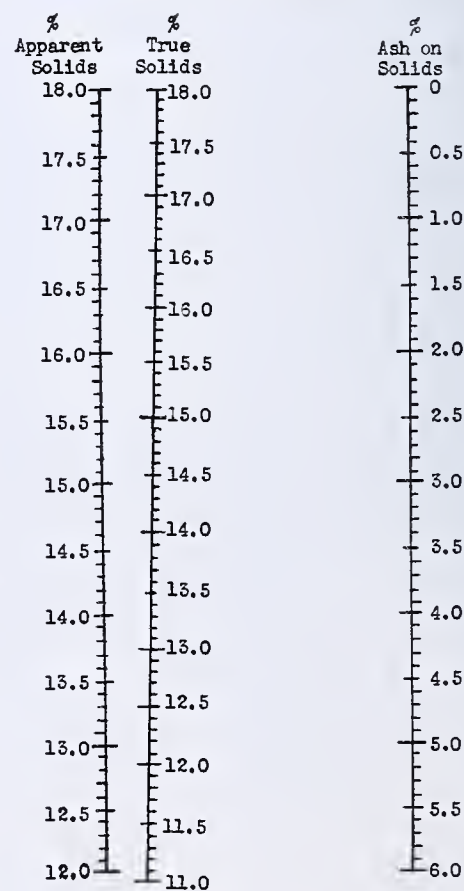


FIGURE 2. NOMOGRAPH

many different soils of distinct types with varied fertilization and drainage, and the different cane varieties included those with both high- and low-ash characteristics. In any case it seems probable that the application of the principles used in this study will yield a factor at any given location which can be used to estimate the true solids from the determined apparent solids and ash with satisfactory accuracy.

To find what accuracy might be expected from the use of the conversion values as given in Table III, they were applied to the published work of Lauritzen and Balch (8) on storage of cane.

In their report are data for apparent and true solids and the ash on about 60 crusher juices. As the ash was given as per cent on true solids, it was first recalculated to the apparent solids basis. Then using the tabulated corrections to estimate the true solids from the apparent solids and ash, it was found that the values obtained for the true solids agreed with the amounts reported, with an average deviation of only ± 0.03 per cent solids. Comparing the small amount of this error with the large difference between apparent and true solids, the approximation of true solids by this method gives, even in the case of individual tests, a figure which represents the true facts rather closely. A more careful determination, especially of the apparent solids, will make the estimation of true solids of individual samples still more accurate. This can be done, for example, by taking the readings only at the temperature for which the hydrometer is calibrated, thus eliminating the use of the correction tables which are also falsely based on pure sucrose solutions.

While it is possible that the exact value of these factors will be different in other sugar-producing territories, some indication that they may not vary significantly was obtained by a further study of the data reported by King (7) on Philippine molasses. His data for ash were recalculated to per cent on apparent solids. Then dividing the reported differences between apparent and true solids by the per cent of ash and then by the per cent of apparent solids and finding a weighted average of the resulting factors, the figure 0.01079 was obtained. This is practically identical with the factor 0.01080, which was found for the Louisiana sirups. In the work of King, as in this study, the sirups or molasses were first diluted to near juice density before analyzing. If the apparent solids had been determined at high density the relationships would have been different.

Considering the large difference which exists between apparent and true solids, especially when the ash content or solids are high, it is evident that the factory records of losses and efficiency are much in error when only the apparent values are used. A discussion of this point by Hill (5) gives examples of such misleading results. In spite of such results, the use of the densimetric methods by the sugar industry and by workers in the agronomic phases of sugar-plant research has been almost universal. This is in part due to the cheapness, speed, and simplicity of the methods for apparent solids as compared with the expensive equipment and time needed to determine solids by drying. While to utilize the procedure just presented for estimating true solids involves the additional determination of ash, this should not require a large number of tests per day, as the ash on a composite sample of each product for each period for which records are made up should be accurate enough to derive the solids correction to be used. In a similar manner, in research work where the data from several tests for solids are to be averaged it is only necessary to find the ash on a composite of the samples to be averaged.

As a development of this method of approximating true solids, the true purity can be closely estimated using calculated true solids and a corrected sucrose value. The difference between apparent and true sucrose varies with the per cent of reducing sugars and to a lesser degree with their composition. To obtain an approximate true sucrose from the apparent value average correction values found for different apparent purities may be used. A more complete discussion of these sucrose conversion values will be made at a future time. As a preliminary example the figure 0.30 was found as the average difference between apparent and true sucrose for crusher juices with an average of 80 per cent apparent purity. When this amount was added to the apparent sucrose

TABLE III. CORRECTIONS FOR CONVERTING APPARENT TO TRUE SOLIDS OF CRUSHER JUICES

(Subtract the proper correction from the determined apparent solids.)

% Apparent Solids % Ash on Solids	14.0	14.5	15.0	15.5	16.0	16.5	17.0	17.5	18.0
2.0	0.34	0.35	0.36	0.38	0.39	0.40	0.41	0.42	0.44
2.2	0.37	0.39	0.40	0.41	0.43	0.44	0.45	0.46	0.47
2.4	0.41	0.42	0.44	0.45	0.47	0.48	0.49	0.51	0.52
2.6	0.44	0.46	0.47	0.49	0.50	0.52	0.54	0.55	0.57
2.8	0.48	0.49	0.51	0.53	0.54	0.56	0.58	0.59	0.61
3.0	0.51	0.53	0.55	0.56	0.58	0.60	0.62	0.64	0.65
3.2	0.54	0.56	0.58	0.60	0.62	0.64	0.66	0.68	0.70
3.4	0.58	0.60	0.62	0.64	0.66	0.68	0.70	0.72	0.74
3.6	0.61	0.63	0.66	0.68	0.70	0.72	0.74	0.76	0.79
3.8	0.64	0.66	0.69	0.71	0.74	0.76	0.78	0.81	0.83
4.0	0.68	0.70	0.73	0.75	0.78	0.80	0.82	0.85	0.87
4.2	0.71	0.74	0.76	0.79	0.81	0.84	0.87	0.89	0.92
4.4	0.75	0.77	0.80	0.83	0.85	0.88	0.91	0.93	0.96
4.6	0.78	0.81	0.84	0.86	0.89	0.92	0.95	0.98	1.00
4.8	0.81	0.84	0.87	0.90	0.93	0.96	0.99	1.02	1.05

reported by Lauritzen and Balch (8) and the resultant approximate true sucrose divided by the calculated true solids, the estimated true purities agreed with those determined with an average deviation of ± 0.70 . Since for this purity the usual difference between apparent and true purity is about 5.00 per cent, this apparently rather poor agreement appears satisfactory. These samples varied widely in purity, and much better results will be obtained when the proper average sucrose correction value for each purity is used.

Summary

The difference between the apparent and true solids of crusher juices and of the sirups produced therefrom can be arithmetically correlated with the ash content. By use of factors determined for this relationship it is possible to estimate the true solids from the determined apparent solids and the per cent of ash on solids. For the raw juices the factor found was 0.0120 and for sirups 0.0108. When the proper factor is multiplied by the per cent of ash on solids and the per cent of apparent solids, one obtains the estimated difference between the apparent and true solids. The subtraction of this product from the observed apparent solids yields the approximate true solids. The accuracy of this estimation is principally dependent on the accuracy of the apparent solids determination, and the calculated true solids seem to agree with that determined within the normal limits obtainable in this determination. These factors may apply only to Louisiana, but there is some evidence that factors of similar value may hold generally. The method of deriving the factors is described, and a table and nomograph are given for rapidly estimating the "true" solids from observed apparent solids and ash. The possibility of approximating the true purity of juices, by use of a corrected apparent sucrose and the estimated "true" solids, is discussed.

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Determination of Chromium, Vanadium, and Molybdenum in Silicate Rocks

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IN THE following there is described a method for the determination of chromium, vanadium, and molybdenum in silicate rocks, which is less laborious and time-consuming than that of Hillebrand (6) and which, in spite of the smaller sample required, can be used for the estimation of smaller amounts of these elements than is possible by the Hillebrand method. A total sample of 1 gram suffices for the determination of as little as 0.001 per cent of vanadium, 0.001 per cent of chromium, and 0.0001 per cent of molybdenum. The chief novelty in the proposed method lies in the determination of vanadium.

The determination of traces of these elements is not of great importance in ordinary rock analysis but is required in special studies, as, for example, those concerned with the geochemical distribution of the elements named.

Outline of the Method

The sample is decomposed in the usual manner by fusion with sodium carbonate, the melt is leached with water, alcohol is added to reduce the manganate, and the mixture is filtered. The filtrate, containing chromate, vanadate, and molybdate, is diluted to the mark in a volumetric flask. If more than 0.01 or 0.02 per cent of chromium is present, this element can be determined directly in the usual manner by comparing the color intensity of the solution with that of a standard potassium chromate solution. For the determination of vanadium, a suitable aliquot portion of the solution is taken, neutralized to methyl orange with sulfuric acid, and extracted with chloroform after the addition of an acetic acid solution of 8-hydroxyquinoline. Chromate does not react with 8-hydroxyquinoline, whereas vanadate forms a compound with the reagent which is extracted by the chloroform, thus leaving chromium in the aqueous solution. The chloroform extracts are evaporated to dryness, and the residue is fused with sodium carbonate to convert vanadium into sodium vanadate, which is dissolved in water. The solution so obtained is treated with phosphotungstic acid to form phosphotungstovanadic acid which possesses an intense yellow to orange color and can thus be determined colorimetrically by comparison against a vanadate solution of known concentration similarly treated.

If the chromium content of the sample is very small, the colorimetric comparison against chromate leads to inaccurate results in most cases because of the presence of traces of foreign substances, chiefly iron, which impart a slight color to the solution. In such cases, a small aliquot portion of the sodium carbonate leach is neutralized with sulfuric acid, treated with 8-hydroxyquinoline, and the solution extracted with chloroform to remove vanadium. Chromium is then determined in the solution from which vanadium has been removed, by the addition of diphenylcarbazide and sulfuric acid and comparison of the red-violet color (of the diphenylcarbazide oxidation compound) with that of a known chromate solution treated in the same way.

Molybdenum is determined in another aliquot portion of the solution by acidification with hydrochloric acid, addition of potassium thiocyanate and stannous chloride, extraction of the

A colorimetric method is described for the determination of chromium, vanadium, and molybdenum in silicate rocks in amounts as small as 0.001, 0.001, and 0.0001 per cent, respectively, all in a 1-gram sample, which is decomposed in the usual way with sodium carbonate. Vanadium is determined with phosphotungstic acid after separation from chromium with 8-hydroxyquinoline; in neutral or slightly acid solutions, quinquivalent vanadium reacts with 8-hydroxyquinoline to give a compound that can be extracted from the aqueous solution with chloroform, whereas hexivalent chromium does not react and remains in the aqueous layer. Diphenylcarbazide is used as reagent for chromium, after the separation of the element from vanadium. Molybdenum is determined by the stannous chloride-thiocyanate-ether method without previous separation from the other constituents of the filtered leach of the sodium carbonate melt.

molybdenum thiocyanate with ether, and comparison of the color of the latter with a standard molybdenum thiocyanate solution obtained in a similar manner.

Discussion of the Method

VANADIUM. It has recently been shown by Montequi and Gallego (10; of. 8) that very small amounts of vanadium can be detected by adding an acetic acid solution of 8-hydroxyquinoline to a neutral or very slightly acid vanadate solution and shaking with chloroform. Quinquivalent vanadium reacts with 8-hydroxyquinoline to give a compound soluble in chloroform with a Bordeaux red to black color. The strongly colored substance formed in the test appears to have the formula $(C_9H_6ON)_4V_2O_3$. Attempts made in this laboratory to base a direct colorimetric determination of vanadium on the reaction of Montequi and Gallego were unsuccessful, chiefly

because of the interference of iron. The filtered aqueous extract of the sodium carbonate melt of an igneous rock usually contains traces of iron, which will react with 8-hydroxyquinoline to give a quinolate soluble in chloroform with an intense greenish black color; the sensitivity of this reaction is as great as that for vanadium. No way of preventing the interference of iron could be found that did not simultaneously destroy, or interfere with, the vanadium reaction. Consequently, in the method here described, the reaction between vanadate and 8-hydroxyquinoline has been used for the isolation and concentration of vanadium, which can then be determined colorimetrically by some method in which traces of iron (and other elements) do not interfere.

Before vanadium can be extracted from the aqueous extract of the sodium carbonate fusion, it is necessary to render the solution slightly acid. It was found that the extraction of vanadium is complete, or practically so, at a pH corresponding to the intermediate color of methyl orange—a convenient reference point; the extraction is also complete from a solution neutralized to the intermediate color of bromocresol green. The presence of neutral alkali salts, such as sodium sulfate, does not interfere. Moreover, there is no interference from silica, aluminum, phosphate, arsenate, fluoride, chloride, borate, or chromate—i. e., from those constituents, all or some of which may be present in the filtrate from the sodium carbonate leach of a rock fusion. Ferric iron, hexivalent molybdenum (in small amounts), and uranium accompany vanadium into the chloroform. Tungsten yields a precipitate with 8-hydroxyquinoline in the slightly acid solution which does not appear to be appreciably soluble in chloroform; the tungsten precipitate gathers at the chloroform-

water interface, causing trouble by preventing the coalescence of the chloroform droplets after shaking.

The vanadium in the chloroform extract can easily be converted into sodium vanadate by evaporating the solvent and fusing the residue with sodium carbonate. The isolated vanadium can be determined colorimetrically by the use of a number of reagents giving sensitive color reactions with the element. It was found in the present work that phosphotungstic acid is especially suitable for the purpose. (Winogradow, 14, has used phosphotungstic acid for the colorimetric determination of vanadium in ashes of organisms.) The strongly colored yellow compound that this reagent yields with quinquivalent vanadium in acid solution is presumably phosphotungstovanadic acid. Vanadate gives a yellow color with tungstate alone in slightly acid solution, but the color is much intensified by phosphoric acid. The sensitivity of the phosphotungstic acid reaction for vanadate is several times as great as that with hydrogen peroxide. Moreover, it seems that the yellow color given by the former reagent can be more accurately matched in a colorimetric comparison than can the reddish brown given by hydrogen peroxide. With phosphotungstic acid as reagent it is possible to detect 0.005 mg. of vanadium in 10 ml. of solution when the latter is viewed through a thickness of 5 cm.; by using a blank for comparison, 0.002 mg. of vanadium can be detected under the same conditions. The reaction is best carried out by adding in succession to the neutral or slightly acid vanadate solution, 85 per cent phosphoric acid and sodium tungstate solution; the quantities specified in the procedure provide a sufficient excess of reagent to give the maximum color intensity for such quantities of vanadium as can be present for satisfactory color comparison in 10 ml. The color development is immediate, and the color intensity undergoes no change with the lapse of time. It is therefore possible to make the color comparison by colorimetric titration—i. e., by adding a standard solution of vanadate to the phosphotungstic acid reagent contained in a tube identical with the one holding the unknown until the colors of the two solutions match. This method of comparison is to be preferred to the use of a colorimeter when the amount of vanadium being determined is very small, since the former method is more sensitive.

The results given in Table I serve to indicate the performance of the phosphotungstic acid method for vanadium in pure solutions and in the presence of such substances as have a bearing on the application of the procedure in rock analysis. The values recorded in the table were all obtained by colorimetric titration as described in the procedure, the solutions being contained in 30-ml. cylindrical tubes, 15 cm. in height and with flat bottoms. In most cases the final volume was near 10 ml. Silica, alkali metal salts, fluoride, borate, and arsenate do not interfere. Aluminum and especially ferric iron diminish the color of the phosphotungstovanadic acid and lead to low results, whereas molybdate gives high results. The amount of iron going into the filtrate from the sodium carbonate melt of an igneous rock is too small to cause appreciable error. Molybdenum does not occur in sufficiently large quantities in rocks to introduce any error.

Table II contains the results obtained in the application of the proposed method to a synthetic basic rock with added amounts of vanadium, and also to a few natural rocks to which were added known amounts of the element. The analysis was made as described in the procedure below, the vanadium first being separated with 8-hydroxyquinoline and chloroform. Except in Nos. 11, 19, and 20, the aliquots used corresponded to 0.1 gram of sample. It may be concluded from these results that the method gives values of satisfactory accuracy for V₂O₃ contents ranging from 0.001 to 0.1 per cent. Chromium is without effect. The use of a mixture of sodium carbonate and potassium nitrate, instead of sodium carbonate

alone, for the decomposition of the rock appears to be unnecessary. The amount of vanadium retained by the leached residue from the sodium carbonate fusion appears to be small enough to neglect (No. 6). In a few cases a little difficulty arose from the formation of an emulsion of chloroform and the aqueous solution, this being more prone to occur with the acid rocks.

In the absence of appreciable amounts of chromium, vanadium can be determined with fair accuracy without previous separation with 8-hydroxyquinoline and chloroform if the amount present is not too small. The figures in Table III (obtained with rocks practically free from chromium) indicate the accuracy that may be expected. The values for the direct determination were obtained by acidifying 10 ml. of filtrate corresponding to 0.1 gram of sample and adding phosphotungstic acid. Generally the hues of the comparison solution and the rock filtrate are not the same, and great exactness in matching is not possible. Although the direct method is not recommended, it may be of some value when an approxi-

TABLE I. DETERMINATION OF VANADIUM BY COLORIMETRIC TITRATION WITH PHOSPHOTUNGSTIC ACID AS REAGENT

No.	Addition	Vanadium Taken Mg.	Vanadium Found Mg.	Error Mg.
1		0.003	0.003	0.000
2		0.005	0.004	-0.001
3		0.012	0.012	0.000
4		0.020	0.021	+0.001
5		0.022	0.021	-0.001
6		0.031	0.029	-0.002
7		0.032	0.030	-0.002
8		0.040	0.041	+0.001
9		0.050	0.051	+0.001
10	0.2 gram of Na ₂ SO ₄	0.020	0.019	-0.001
11	0.5 gram of Na ₂ SO ₄	0.025	0.025	0.000
12	1.0 gram of NaCl	0.025	0.023	-0.002
13	0.10 gram of SiO ₂ as sodium silicate + 1 ml. of 6 N H ₂ SO ₄	0.025	0.024	-0.001
14	10 mg. of Al as AlCl ₃	0.025	0.022	-0.003
15	50 mg. of Al as AlCl ₃	0.025	0.017	-0.008
16	0.5 mg. of Fe as FeCl ₃	0.025	0.023	-0.002
17	1.0 mg. of Fe as FeCl ₃	0.025	0.021	-0.004
18	1.0 mg. of Fe as FeCl ₃ + 0.5 ml. of 85% H ₃ PO ₄	0.025	0.021	-0.004
19	10 mg. of NaF + 0.1 ml. of 6 N H ₂ SO ₄	0.025	0.025	0.000
20	0.1 gram of H ₃ BO ₃	0.025	0.025	0.000
21	0.5 mg. of Mo as NH ₄ molybdate	0.020	0.022	+0.002
22	1.0 mg. of Mo as NH ₄ molybdate	0.020	0.023	+0.003
23	10.0 mg. of Mo as NH ₄ molybdate	0.020	0.026	+0.006
24	50 mg. of Na ₂ HAsO ₄	0.025	0.024	-0.001

TABLE II. DETERMINATION OF VANADIUM IN SILICATE ROCKS BY THE 8-HYDROXYQUINOLINE-PHOSPHOTUNGSTIC ACID METHOD

No.	Sample	V ₂ O ₃ Present %	V ₂ O ₃ Added %	V ₂ O ₃ Found %	Error V ₂ O ₃ %
1	Synthetic basic rock ^a	0.000 ^b
2	Synthetic basic rock	0.0021	0.0027	+0.0006
3	Synthetic basic rock	0.004	0.005	+0.001
4	Synthetic basic rock	0.015	0.014	-0.001
5	Synthetic basic rock	0.042	0.040	-0.002
6	Synthetic basic rock	0.060	0.059 ^c	-0.001
7	Synthetic basic rock	0.105	0.110	+0.005
8	Synthetic basic rock	0.105	0.101	-0.004
9	Synthetic basic rock with 1% Cr ₂ O ₃	0.006	0.005	-0.001
10	Synthetic basic rock with 1% Cr ₂ O ₃	0.0120	0.0115	-0.0005
11	Granite (0.5 gram)	0.0015	0.0030	0.0040	-0.0005
12	Granite + 2% F	0.0015	0.0065	0.007	-0.001
13	Gabbro (0.005% Cr ₂ O ₃)	0.019	0.049	0.065	-0.003
14	Gabbro (same as No. 13)	0.022 ^d
15	Diabase	0.029	0.033	0.062	0.000
16	Diabase (same as No. 15)	0.029 ^d
17	Shale	0.044
18	Shale (same as No. 17)	0.041 ^d
19	Magnetite-ilmenite sand (0.01 gram) ^e	0.245
20	Magnetite-ilmenite sand (same as No. 19)	0.23 ^d

^a Percentage composition: SiO₂, 55; Al₂O₃, 20; Fe₂O₃, 10; MgO, 6; CaO, 7; TiO₂, 1; P₂O₅, 0.5; MnO, 0.5.
^b Sensitivity of method for 0.5-gram sample < 0.0005 per cent V₂O₃.
^c Refusion of the washed residue from the first sodium carbonate fusion yielded an additional 0.001 per cent of V₂O₃.
^d Sample fused with Na₂CO₃ + KNO₃ (4 to 1) instead of with Na₂CO₃ alone as in other determinations.
^e Fused 1 hour, instead of 20 to 30 minutes as in other determinations.

mate figure for vanadium in a rock sensibly free from chromium is desired.

CHROMIUM. For the determination of very small amounts of chromium in rocks, the usual method involving the comparison of the color of the filtrate from the sodium carbonate melt with a potassium chromate solution of known concentration is unsatisfactory, not so much because of insufficient sensitivity as on account of interference from traces of foreign substances which impart a color to the solution. It is usually found that the filtered leach of the sodium carbonate melt of a rock possesses a yellow-brown tinge, even when no chromium is present. This slight coloration is probably due largely to colloidal hydrous ferric oxide. If nitrate is used in the fusion and the crucible is attacked, a yellowish coloration may be imparted to the solution by the dissolved platinum. Incomplete reduction of manganate, and failure to wash traces of coloring matter from the filter paper with hot strong sodium carbonate solution may also lead to false coloration of the filtrate, but these sources of error are easily avoided.

The presence of iron in the filtrate seems to result from the peptization of hydrous ferric oxide by silica. The error may be considerable in the case of acid rocks containing relatively much iron. Thus a rhyolite high in iron showed an apparent Cr_2O_3 content of 0.005 per cent by the usual method, when actually no chromium could be detected by the sensitive diphenylcarbazide reaction described below, and a granite gave an apparent percentage of 0.004 Cr_2O_3 when actually only 0.0006 per cent was present. With basic rocks the error may be smaller. For example, a gabbro containing 0.005 per cent of Cr_2O_3 gave an apparent value of 0.007 to 0.008 per cent, and the synthetic basic rock of Table II showed 0.004 to 0.005 per cent instead of the true value, 0.002 per cent.

Therefore, it is desirable to base the colorimetric determination of traces of chromium on the use of a reagent which gives a sensitive specific reaction with the element. Such a reagent is diphenylcarbazide, which, as discovered by Cazeneuve (1), reacts with sexivalent chromium in acid solution to give an intensely colored red-violet oxidation product. A colorimetric

method for chromium has been based on this reaction by Moulin (12) and others. The method does not appear to have been applied to the determination of chromium in silicates, although the reaction is used for the detection of the element in rocks and minerals (2).

In the present work it was found that a fairly satisfactory determination of traces of chromium in silicates could be obtained by the use of diphenylcarbazide. Quinquevalent vanadium interferes by reacting with the reagent in acid solution to give a strongly colored yellow compound. However, vanadium can be removed from the solution as previously described by the addition of 8-hydroxyquinoline and extraction of the vanadium hydroxyquinoline compound with chloroform; sexivalent chromium is not reduced in the process. The excess of 8-hydroxyquinoline is simultaneously extracted by the chloroform from the neutralized solution.

If the amount of V_2O_5 does not exceed the amount of Cr_2O_3 , it is usually unnecessary to remove the vanadium. Although the hue of the chromium-diphenylcarbazide solution is then altered, becoming more red, no appreciable error results.

A brief study was first made of the determination of chromate in pure solution with diphenylcarbazide. Without giving the numerical data obtained, the results may be summarized as follows:

The stability of the red-violet compound formed in the oxidation of the diphenylcarbazide by chromate is good under the proper conditions. Of chief importance is the acidity of the solution, which must be sufficient to permit the development of the maximum color intensity and to prevent the interference of other elements that may give a color at low acidities. A too high acidity leads to fairly rapid fading of the chromate-diphenylcarbazide color. Thus, the color of a solution containing the equivalent of 0.010 mg. of Cr_2O_3 , 5 ml. of 6 *N* sulfuric acid, and 2 ml. of 0.25 per cent diphenylcarbazide in 25 ml. showed a decrease in intensity amounting to 7 or 8 per cent in 1 hour; solutions containing less chromium are more unstable, other conditions being the same. When the acidity was reduced to approximately 0.2 *N* (1 ml. of 6 *N* sulfuric acid in 25 ml. of final volume) the color was more stable. After 1 hour, with the same amount of chromium and reagent as before, the color intensity in this case had decreased by 3 per cent on the average. Moreover, at the lower acidity the color given by low chromate concentrations (0.1 mg. of Cr_2O_3 per liter) was nearly as stable as that of more concentrated solutions.

The excess of diphenylcarbazide has but a small effect on the intensity and stability of the color. Thus, with 0.010 mg. of Cr_2O_3 in 25 ml. of 0.2 *N* sulfuric acid, the color intensity was the same within a few per cent whether the amount of diphenylcarbazide solution used was 2, 1, 0.5, or 0.2 ml. of 0.5 per cent reagent in 1 to 1 acetone, and the color stability was approximately the same in all cases. The reproducibility of the color is not all that might be desired, as illustrated by the following figures (expressing relative color intensities) obtained by adding a mixture of 1 ml. of 0.25 per cent diphenylcarbazide, 1 ml. of 6 *N* sulfuric acid, and 3 ml. of water to 15 ml. of water containing the designated amounts of chromium, and diluting to 25 ml.

0.005 mg. of Cr_2O_3 —1.00, 0.96; 1.00, 1.02
0.010 mg. of Cr_2O_3 —1.00, 1.025, 1.015; 1.00, 1.02, 1.025
0.015 mg. of Cr_2O_3 —1.00, 1.01

Beer's law is followed (Figure 1). The presence of sodium sulfate does not alter the hue or intensity of the chromate-diphenylcarbazide color, even when as much as 5 per cent of the salt is present in the solution.

The results given in Table IV were obtained by following the directions given in the procedure. Chromium was added to the samples in the form of chromic sulfate. The method proposed gives, on the whole, satisfactory results. There is a distinct tendency for the chromium values to be slightly low. The color of the filtered sodium carbonate leach of the rock, after removal of vanadium and addition of diphenylcarbazide, usually does not have exactly the same hue as that of the standard chromate solution. The difference is most marked at very low chromium concentrations; then the sample solution generally possesses a distinct brownish tinge, in contrast to the

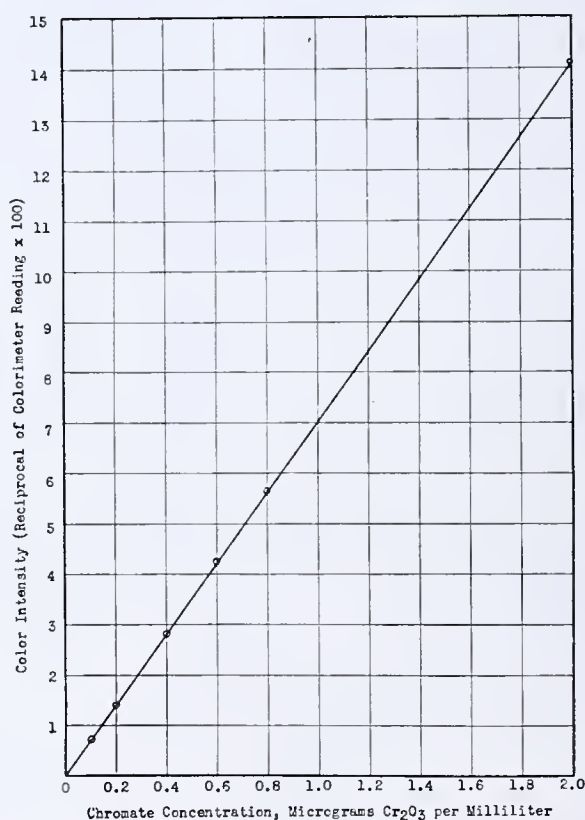


FIGURE 1. RELATION BETWEEN CHROMATE CONCENTRATION AND COLOR INTENSITY IN DETERMINATION OF CHROMIUM BY THE DIPHENYLCARBAZIDE METHOD

pure red-violet of the comparison solution. At higher chromium concentrations the difference in hue is very slight and rarely gives any trouble. As little as 0.0005 per cent of Cr₂O₃ can be detected when a 0.1-gram sample is taken and vanadium is first removed.

TABLE III. DETERMINATION OF VANADIUM IN ROCKS WITHOUT PREVIOUS SEPARATION WITH 8-HYDROXYQUINOLINE AND CHLOROFORM

No.	Sample	V ₂ O ₅ Found		Difference, V ₂ O ₅
		8-Hydroxy-quinoline method	Direct method	
		%	%	%
1	Synthetic basic rock	0.042	0.036	-0.006
2	Synthetic basic rock	0.105	0.11	+0.005
3	Diorite	0.026	0.023	-0.003
4	Gabbro (0.005% Cr ₂ O ₃)	0.019	0.022	+0.003
5	Gabbro (0.005% Cr ₂ O ₃)	0.065	0.06 to 0.07	±0.005
6	Diabase	0.029	0.031	+0.002
7	Diabase	0.062	0.055	-0.007
8	Shale	0.044	0.039	-0.005
9	Magnetite-ilmenite sand	0.245	0.245	0.00

TABLE IV. DETERMINATION OF CHROMIUM IN ROCKS WITH DIPHENYL CARBAZIDE

No.	Sample	Cr ₂ O ₃ Present	Cr ₂ O ₃ Added	Cr ₂ O ₃ Found	Error Cr ₂ O ₃
		%	%	%	%
1	Synthetic basic rock ^a	0.002	0.005	0.0065	-0.0005
2	Synthetic basic rock	0.002	0.005	0.007	0.000
3	Synthetic basic rock ^b	0.002	0.010	0.012	0.000
4	Synthetic basic rock	0.002	0.020	0.023	+0.001
5	Synthetic basic rock ^b	0.002	0.020	0.022	0.000
6	Synthetic basic rock	0.002	0.050	0.053	+0.001
7	Synthetic basic rock	0.002	0.050	0.053	+0.001
8	Synthetic basic rock + 0.10% V ₂ O ₅ ^b	0.002	0.005	0.0065	-0.0005
9	Synthetic basic rock + 0.10% V ₂ O ₅ ^b	0.002	0.050	0.050	-0.002
10	Rhyolite (V ₂ O ₅ = nil) ^{b, c}	0.000	0.0010	0.0008	-0.0002
11	Rhyolite ^{b, c}	0.000	0.0020	0.0016	-0.0004
12	Rhyolite ^b	0.000	0.0020	0.0017	-0.0003
13	Rhyolite ^b	0.000	0.0050	0.0044	-0.0006
14	Rhyolite	0.000	0.0050	0.0050	0.0000
15	Rhyolite + 0.05% V ₂ O ₅ ^b	0.000	0.002	0.001	-0.001
16	Rhyolite + 0.10% V ₂ O ₅ ^b	0.000	0.002	0.0015	-0.0005
17	Rhyolite + 0.10% V ₂ O ₅ ^b	0.000	0.000	0.000	0.000
18	Granite ^b	0.0006	0.0020	0.0025	0.000
19	Gabbro (0.02% V ₂ O ₅) ^b	0.005	0.010	0.014	-0.001
20	Gabbro (0.12% V ₂ O ₅) ^b	0.005	0.000	0.0045	-0.0005
21	Gabbro (0.12% V ₂ O ₅) ^b	0.005	0.010	0.0135	-0.0015

^a For composition, see Table II; 0.2-gram sample used in No. 1, 0.1 gram in all other determinations.
^b Treated with 8-hydroxyquinoline and extracted with chloroform; others not so treated.
^c Chromium (as chromate) added to filtrate of leached melt; in all others, chromium added before fusion.

MOLYBDENUM. For the colorimetric determination of this element in silicate rocks, a very sensitive reaction must be made the basis of the method, since the amount of MoO₃ present may be no more than 0.001 to 0.0001 per cent.

Attempts to make use of potassium ethyl xanthate (9) as reagent for the purpose resulted unsatisfactorily in the author's hands, as has also been the experience of others. Phenylhydrazine (11) is not well suited for the determination of very minute amounts of molybdenum because of insufficient sensitivity. (von Hevesy and Hobbie, 5, in a paper on the determination of tungsten and molybdenum in rocks have described the determination of molybdenum with phenylhydrazine as colorimetric reagent; these authors used samples weighing from 150 to 270 grams for molybdenum contents in the range 10⁻⁴ to 10⁻³ per cent.) The familiar potassium thiocyanate-stannous chloride method for molybdenum was, however, found excellent for the minute amounts of the element occurring in igneous rocks. (Stanfield, 13, has applied this method to the determination of molybdenum in plant ashes and soils, first isolating the element as the sulfide and finally extracting the molybdenum thiocyanate with butyl acetate. Hauptmann and Balconi, 4, have used both the thiocyanate-stannous chloride method, without an extractant, and the phenylhydrazine method for the determination of small amounts of molybdenum in manganese minerals.) The reaction can be applied directly to the filtered leach of the sodium carbonate melt of the sample. By using ethyl ether to extract the molybdenum thiocyanate compound from the aqueous solution,

the stability of the colored product is increased, and at the same time the substance is concentrated in a small volume of solvent, so that the determination of extremely small amounts of molybdenum becomes possible. In this way as little as 0.001 mg. of the element can be determined in 100 ml. of solution. Rhenium gives the same reaction as molybdenum (3), but it may be expected that this element will not be present in detectable amounts in silicate rocks. It is advantageous to make the colorimetric determination of the molybdenum thiocyanate in the ether by colorimetric titration: adding a standard ethereal solution of molybdenum thiocyanate to pure ether having nearly the same volume as the unknown solution and contained in an identical tube, until the colors match. By using color-comparison tubes of suitable size, it is possible to determine as little as 0.0001 per cent of molybdenum trioxide when a 0.5-gram sample is taken. Ethyl ether is not an ideal solvent for the extraction and for making up the standard molybdenum solution, because of its volatility. However, there are certain objections to the use of other solvents, such as butyl acetate and cyclohexanol as shown by Hurd and Allen (7), and therefore ethyl ether was employed in the present work; it is satisfactory if reasonable care is taken in its use.

The method proposed was tested with synthetic mixtures, simulating acid and basic rocks, to which known amounts of molybdenum were added, and also with rocks of various types. The results are tabulated in Table V. Other elements do not, in general, interfere. The major rock constituents, including phosphorus, are without effect; chromium, vanadium, uranium, tungsten, tantalum, and fluorine do not interfere, at least in the amounts that these are met with in silicate rocks. Much fluoride leads to low results. Small amounts of iron, such as may be found in the sodium carbonate filtrate, give no coloration when the directions given below are followed, as was proved by the addition of 0.5 mg. of iron as the chloride.

Any separation of silica after acidification of the filtrate leads to low results, presumably because of the adsorption of molybdenum. It was feared that traces of platinum might interfere, since chloroplatinous acid is soluble in ether with a yellow color; however, thiocyanate reduces the sensitivity of this reaction. Blanks showed that there is no significant error due to slight attack of the platinum crucible by the sodium carbonate melt. Tungsten in appreciable amounts (0.05 per cent) appears to alter the hue of the ether solution of the molybdenum thiocyanate, making it more yellow, and thus renders the color comparison less exact. The small amounts of tungsten usually encountered in igneous rocks do not interfere. Even in the absence of tungsten, differences in hue between the unknown and standard solutions were sometimes noted. In every case in which there was a difference, the standard possessed a more orange tint. These differences were usually slight, and in no case, is it believed, was an error greater than ±10 per cent introduced on this account; therefore the cause, or causes, of the difference in hue was not investigated. It is important that the ether used for diluting the standard molybdenum thiocyanate solution be shaken with stannous chloride and potassium thiocyanate before use; ether not so treated is likely to bleach the color of the molybdenum thiocyanate and give a decided reddish hue to the normal yellow-brown color of the standard. The standard solution is not stable; it becomes darker on standing.

In determining minimal quantities of molybdenum by this method, it is important to run a blank on the sodium carbonate used for the decomposition; in the most accurate work only sodium carbonate showing a negligible blank should be employed. The c. p. anhydrous sodium carbonate of one manufacturer gave a blank corresponding to 3.5 ± 1 × 10⁻⁵ per cent of MoO₃, whereas the product of another gave a barely detectable reaction corresponding to 1 × 10⁻⁵ per cent of MoO₃.

There appears to be no appreciable retention of molybdenum by the leached residue, at least for amounts in the range of 0.01 to 0.0001 per cent of MoO₃.

TABLE V. DETERMINATION OF MOLYBDENUM IN ROCKS BY THE THIOCYANATE-STANNOUS CHLORIDE-ETHER METHOD

No.	Sample	MoO ₃ Present %	MoO ₃ Added %	MoO ₃ Found %	Error, MoO ₃ %
1	Synthetic acid rock (0.5 gram) ^a	0.0000	...
2	Synthetic acid rock (0.5 gram)	0.0000	0.00070	0.00075	+0.00005
3	Synthetic acid rock (0.1 gram)	0.0000	0.010	0.009	-0.001
4	Synthetic basic rock (0.5 gram) ^b	0.0000	...
5	Synthetic basic rock (0.5 gram)	0.0000	0.00040	0.00045	+0.00005
6	Synthetic basic rock (0.1 gram)	0.0000	0.007	0.006	-0.001
7	Granite (0.1 gram)	0.0003	0.007	0.008	+0.001
8	Granite + 10% P ₂ O ₅ (0.1 gram)	0.0003	0.007	0.008	+0.001
9	Granite + 0.5% F (0.1 gram)	0.0003	0.007	0.007	0.000
10	Granite + 1.3% F (0.1 gram)	0.0003	0.007	0.0055	-0.002
11	Granite + 0.5% U + 1% Ta (0.1 gram)	0.0003	0.007	0.0075	0.000
12	Diorite (0.5 gram)	0.0001	0.00055	0.0006	-0.00005
13	Diorite (0.5 gram)	0.0001	0.0002	0.00025	-0.00005
14	Diorite (0.5 gram)	0.0001	0.0002	0.00035	+0.00005
15	Gabbro (0.5 gram)	0.00015	0.0003	0.0005	-0.00005
16	Gabbro (0.5 gram)	0.00015	0.0007	0.00075	-0.0001
17	Slate	0.00005	0.00055	0.00055	-0.00005
18	Synthetic acid rock + 0.5% F (0.5 gram)	0.0000	0.0007	0.0008	+0.0001
19	Synthetic acid rock + 0.05% WO ₃	0.0000	0.0007	0.0009	+0.0002

^a Percentage composition: SiO₂, 77; Al₂O₃, 17; Fe₂O₃, 2.1; MgO, 1.3; CaO, 2.2; TiO₂, 0.2; P₂O₅, 0.1; MnO, 0.1.

^b For composition see Table II.

^c Molybdenum added to filtrate of sodium carbonate melt; in all other determinations element added to sample before fusion.

Procedure

DECOMPOSITION OF SAMPLE. Weigh 1 gram of 100-mesh rock powder into a platinum crucible and mix with four to five times as much powdered anhydrous sodium carbonate (reagent quality). Cover the crucible, heat to fusion, and keep at the full heat of a Meker burner for 20 to 30 minutes, or longer if relatively much chromite or magnetite is present. Allow the crucible to cool to room temperature, add a few milliliters of water to cover the melt, and then warm with a small flame to loosen the cake. Transfer the cake to a small Pyrex beaker, rinse the crucible with hot water, add 2 to 5 drops of ethyl alcohol (depending upon the amount of manganate present) and 30 or 40 ml. of water to the beaker, and heat on the steam bath. During the digestion aid the disintegration of the cake by crushing and grinding with a glass rod flattened at one end. When the residue has been well disintegrated and the manganate reduced, filter the liquid through a small fine-grained filter paper which has been previously washed with hot 20 per cent sodium carbonate solution to remove traces of coloring matter. Wash the insoluble material in the beaker and on the paper with hot 1 per cent sodium carbonate solution (four or five 5-ml. portions will usually suffice).

If the filtrate has a distinct yellow color, determine chromium in the combined filtrate and washings by the usual method of comparison against a standard solution of potassium chromate containing sodium carbonate, using a colorimeter or Nessler tubes, depending on the strength of color. For chromium contents less than 0.01 or 0.02 per cent of Cr₂O₃, the value thus obtained may be appreciably in error and it is then better to determine chromium with diphenylcarbazide as described below.

VANADIUM. Special solutions are prepared as follows:

8-Hydroxyquinoline, 2.5 per cent. Dissolve 2.5 grams of finely powdered 8-hydroxyquinoline in 100 ml. of 2 *N* (1 to 8) acetic acid.

Sodium tungstate, 5 per cent. Dissolve 5 grams of Na₂WO₄·2H₂O (reagent quality) in 100 ml. of water.

Standard vanadium solution. Prepare a solution of ammonium metavanadate (or other alkali vanadate) containing the equivalent of approximately 0.01 mg. of V₂O₅ per ml. by diluting a stronger solution. Standardize the stronger solution in the usual manner by reducing the acid solution with sulfur dioxide and titrating with standard potassium permanganate after expulsion of sulfur dioxide.

Make up the combined filtrate and washings from above to 100 ml. in a volumetric flask. For the determination of vanadium, transfer 10 to 25 ml. of this solution, depending upon the probable vanadium content (for basic and intermediate rocks such as diabases, gabbros, and diorites, 10 ml., corresponding to 0.1 gram of sample, will usually suffice, whereas for acid rocks—e. g., granites—25 ml., or better 50 ml., should be taken) to a 50-

or 100-ml. Erlenmeyer flask, and add one drop of methyl orange indicator solution. Then add 4 *N* sulfuric acid carefully from a buret until the solution assumes the intermediate color of the indicator; make a note of the volume of acid required if chromium is to be determined later with diphenylcarbazide. Swirl the liquid to liberate carbon dioxide present in supersaturated solution, and transfer the solution to a small separatory funnel. Add 2 ml. of chloroform (analytical reagent) and 0.1 ml. of 8-hydroxyquinoline solution. Shake moderately vigorously for 1 minute, allow the layers to separate, and draw off the chloroform into a platinum crucible; add 1 ml. of chloroform to wash out the stem of the funnel. Then add 2 ml. of chloroform and 0.1 ml. of 8-hydroxyquinoline to the solution in the funnel, shake as before, and transfer the chloroform to the platinum crucible. Repeat the extraction once more with chloroform and 8-hydroxyquinoline. A total of three extractions should suffice for the majority of rocks. The last chloroform extract should show only a faint yellowish coloration due to 8-hydroxyquinoline itself.

To the crucible containing the combined chloroform extracts add 0.10 gram of anhydrous sodium carbonate, and evaporate to dryness at a low temperature. Then heat the crucible with a flame to destroy organic matter, finally applying the full heat of the burner for 1 or 2 minutes. Cool, add 3 or 4 ml. of water, let stand until solution is complete (warming, if desired, to hasten dissolution), and transfer the solution to a color-comparison tube. It is convenient to use a tube having an internal diameter of 1.5 cm. and a length of 15 or 16 cm.; if the vanadium content of the sample is very small (<0.005 per cent of V₂O₅), it is preferable to use a narrower tube to increase the precision of the color comparison. Rinse out the crucible with one or two portions of water of a few milliliters each so that the total volume of the solution will be 8 or 10 ml. The solution should be colorless and free from any marked turbidity; if the liquid is appreciably turbid, filter it through a sintered glass or porcelain filter crucible, not through paper.

To a second identical tube add 0.10 gram of sodium carbonate and slightly less water, by a few milliliters, than there is solution in the first tube. Then add the following in succession to both tubes, mixing after each addition: 1 ml. of 4 *N* sulfuric acid (free from reducing substances), 0.1 ml. of 85 per cent phosphoric acid, and 0.2 ml. of sodium tungstate solution. Now, add standard vanadate solution from a buret to the comparison solution until, after mixing, the colors of the two solutions match when the tubes are viewed axially against a white background. Near the end point, water should be added to the solution having the lesser volume until both tubes contain approximately the same volume of liquid.

CHROMIUM (WITH DIPHENYLCARBAZIDE). Special solutions are prepared as follows:

Diphenylcarbazide, 0.25 per cent. Dissolve 0.05 gram of powdered diphenylcarbazide in 10 ml. of acetone (reagent quality) and dilute with 10 ml. of water. This solution becomes yellow-brown on standing, and is best prepared the same day that it is used.

Standard chromium solution. Prepare a solution of potassium chromate containing the equivalent of 0.001 mg. of Cr₂O₃ per milliliter by diluting a stronger solution obtained by weighing out pure dry potassium chromate ($\frac{2K_2CrO_4}{Cr_2O_3} = 2.55$).

The following directions apply to samples containing less than 0.05 per cent of Cr₂O₃.

Transfer 10 ml. of the diluted filtrate and washings of the decomposed rock (corresponding to 0.1 gram of sample) to a small separatory funnel and, without using an indicator, add the volume of 4 *N* sulfuric acid required to neutralize the solution to methyl orange as determined under Vanadium or in a blank, and swirl for a minute or two to liberate excess carbon dioxide. Then add 0.1 ml. of 2.5 per cent 8-hydroxyquinoline in 2 *N* acetic acid, and extract three times with 2-ml. portions of chloroform (without adding any additional hydroxyquinoline between extractions), discarding the chloroform extracts. (If it is known that the amount of vanadium does not exceed the amount of chromium, omit the treatment with 8-hydroxyquinoline.) The last chloroform extract should be colorless; if it is not, extract further. To remove chloroform droplets from the aqueous solution, filter the latter through a small (5-cm.) moist filter paper previously washed with water, and receive the filtrate in a 25-ml. volumetric flask. Wash the separatory funnel and the filter with a few small portions of cold water, taking care that the total volume of filtrate and washings does not exceed 20 ml.

Add all at once a mixture of 1 ml. of diphenylcarbazide solution, 1 ml. of 6 *N* sulfuric acid, and 2 or 3 ml. of water to the filtrate and washings in the volumetric flask, mix, make up the

volume to 25 ml. with water, and compare in a colorimeter against a standard chromate solution similarly treated. For samples containing up to 0.02 per cent of Cr_2O_3 a convenient concentration of standard solution is 0.01 mg. of Cr_2O_3 per 25 ml. of final volume after treatment with acidified diphenylcarbazide. The sample and standard solutions should be treated with diphenylcarbazide at the same time, and the comparison made without undue delay, since the red-violet color of the oxidized reagent fades slowly on standing. The color development is very rapid and the solutions may therefore be read in the colorimeter as soon as they have been well mixed. It is not necessary to add sodium carbonate to the standard solution.

If the amount of chromium present is less than 0.002 or 0.003 per cent of Cr_2O_3 , the color comparison cannot well be made with a colorimeter. In such a case transfer the vanadium-free solution of the sample which has been treated with diphenylcarbazide to a color comparison tube (see under Vanadium), and add to a similar tube 1 ml. each of diphenylcarbazide solution and 6 *N* sulfuric acid diluted with water to give approximately the same volume as that of the unknown. Then make the color comparison by adding from a buret a standard chromate solution treated with diphenylcarbazide to the comparison solution until the liquids in the tubes show the same color intensity when viewed against a white background from above. The standard solution may conveniently contain 0.01 mg. of Cr_2O_3 per 25 ml. of final volume.

MOLYBDENUM. Special solutions are prepared as follows:

Potassium thiocyanate, 5 per cent.

Stannous chloride. Ten grams of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 ml. of 1 to 9 hydrochloric acid. This solution should be freshly prepared.

Standard molybdate solution, 0.05 mg. of MoO_3 per ml. Prepare by diluting an ammonium molybdate solution 10 or 20 times as strong. Obtain the exact strength of the stronger solution by standardization—for example, by precipitating as lead molybdate.

Ethyl ether, treated with thiocyanate and stannous chloride. Shake reagent quality ether with one-tenth its volume of equal amounts of potassium thiocyanate and stannous chloride solutions the same day it is to be used.

Transfer 50 ml. of the diluted filtrate and washings from the sodium carbonate melt (corresponding to 0.5 gram of sample) to a separatory funnel of suitable size, add slowly with agitation 8 ml. of concentrated hydrochloric acid, swirl to liberate excess carbon dioxide, and cool the solution to 20° . Add 3 ml. of potassium thiocyanate solution, mix, and then add 3 ml. of stannous chloride solution; after mixing allow the solution to stand for 30 to 45 seconds. Add 6 or 7 ml. of reagent quality ethyl ether to the separatory funnel, shake vigorously for 30 seconds, allow the liquids to separate, draw off the aqueous layer into a beaker, and run the ether into a color-comparison tube having a diameter of approximately 10 mm. (a small vial, 14×55 mm., can be used for the purpose). Return the aqueous solution to the separatory funnel, extract with 2 or 3 ml. of ether, and add the latter to the first extract in the comparison tube.

Usually, for the amounts of molybdenum likely to be encountered in rocks, two extractions with ether will suffice. However, it is best to extract a third time and examine the ether layer in the funnel for a trace of color by looking through the great thickness, and to add this extract to the others if any color is apparent. To make the color comparison, add the standard ethereal solution of molybdenum thiocyanate (prepared as described below) from a microburet to a second identical tube containing an appropriate volume of ether, treated with thiocyanate and stannous chloride, until the colors match when the tubes are viewed from above against a white background. Run a blank on the sodium carbonate used through all the steps of the procedure.

To prepare the standard molybdenum thiocyanate solution, transfer 5 ml. of ammonium molybdate solution, containing 0.05 mg. of MoO_3 per ml., and 50 ml. of 5 per cent sodium carbonate solution to a separatory funnel, add carefully 8 ml. of concentrated hydrochloric acid, swirl to liberate excess carbon dioxide, and cool to 20° C. Then add 3 ml. each of potassium thiocyanate and stannous chloride solution, in the order named, mixing well after each addition. After 30 to 45 seconds extract with 10 ml. of ether and run the latter into a dry 25-ml. volumetric flask. Extract four times more with 5-ml. portions of ether (the last extract should be nearly colorless) and add the extracts to the flask. Make up the combined extracts to 25 ml. with ether that has been shaken with thiocyanate and stannous chloride. There is thus obtained a solution containing the equivalent of 0.01 mg. of MoO_3 per ml. Take great care to prevent changes in concentration of the standard solution as a result of evaporation; transfer the solution rapidly to the microburet and keep the latter well covered. Because of its instability, the solution cannot be kept longer than a day.

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A Spindle for Insulating Wires

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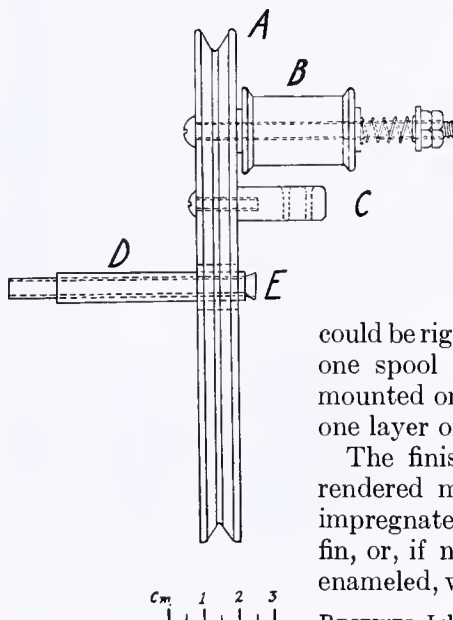
IN THE construction of thermocouples and other electrical apparatus it is sometimes desirable to wrap a small bundle of wires with cotton or silk insulating thread. This is a rather tedious procedure when done by hand, but the simple and easily constructed spindle illustrated enables one to wrap about a foot of wire with one layer of thread in a minute.

On a pulley, *A*, are mounted a spool, *B*, and a guide, *C*, at about the same distance from the center. The spool carries the thread to be used, and is supported by a machine bolt carrying a spring so that the tension on the thread may be adjusted. The bundle of wires to be wrapped is inserted in a glass guard, *E*, within the stationary hollow axle, *D*. The pulley is driven

by a small motor, whose speed is conveniently controlled by a foot-operated rheostat of the type used with sewing machines. If a large amount of winding is to be done, an automatic feed for the wire

could be rigged up. Also, more than one spool and guide could be mounted on the pulley if more than one layer of insulation was desired.

The finished bundle may be rendered moisture-proof by being impregnated with shellac or paraffin, or, if none of the conductors is enameled, with glyptal varnish.



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Handling and Weighing Absorption Tubes in Microdeterminations of Carbon and Hydrogen

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THE standard method of handling and weighing absorption tubes in microanalysis is that of Pregl (14). This method was an excellent beginning. However, in an effort to remove possible errors, various workers have developed improvements of definite value, mainly along two lines: to find better absorption agents, and to produce a tube which could be closed to the atmosphere.

The original absorption agents, calcium chloride and soda lime, have been almost entirely replaced now by magnesium perchlorate (8, 10, 12) and ascarite. The anhydrous granular magnesium perchlorate has almost double the moisture-absorbing capacity of the trihydrate salt and is the preferable form to use.

In an attempt to make it possible to close the tube to the atmosphere, tubes have been made, the ends of which could be closed by mercury seals (5, 10), by hollow ground-glass stoppers (2, 6, 7), and by wires (4, 13). A recent development has a special absorption tube, designed and described by Friedrich (8), in which a single stopcock closes both the entrance and the exit to the tube.

The method of handling absorption tubes used in this laboratory has been developed during the course of making several thousand carbon and hydrogen determinations, and although there may be few separate operations which are new, the method, as a whole, has been found to be a distinct improvement over the regular method given by Pregl (14).

The principal difficulties encountered in this laboratory in handling and weighing absorption tubes have been (1) lack of constancy in temperature, (2) long conditioning time of Pregl tubes beside the balance, (3) the certain removal of lint and dirt from glass surfaces, and (4) elimination of static charge from glass surfaces.

Constancy of Temperature

Constant temperature proved to be an important factor in both handling and weighing of absorption tubes. A constant-temperature room was to be desired but, if sudden fluctuations were avoided, a gradual change in temperature did not seem to affect the weighings noticeably. The balances in this laboratory were placed in a separate room which opened into the main laboratory. This room had inside walls only, with no ventilation except through the doorway which was kept open to the main laboratory. The temperature in this room fluctuated very little but still tended to be near that of the outside room. There were no drafts. A constant zero point on the balances was obtained, except on abnormal days when the outside temperature variation was very large.

Conditioning Time

The regular tubes as designed by Pregl (14) have been chosen as the most practical absorption apparatus, for the tubes are of such simple construction that they are easily prepared for weighing. The main criticism advanced against the Pregl tubes has been the fact that they are open to the atmosphere from 10 to 20 minutes during conditioning beside the balance. In this laboratory the tubes picked up weight during this period of time. The amount of increase was found

to be determined by changes in the temperature, by the percentage of moisture in the air, and by the length and diameter of the constrictions in the ends of the tubes. Lieb and Soltys (11) have demonstrated the importance of constrictions of the proper size. In this laboratory absorption tubes with constrictions 0.15–0.20 mm. in diameter and 4 mm. long have always been used.

Both tubes were wiped and placed on the rack beside the balance, the water tube being first, and were then weighed in the same order. The time interval on each tube between completion of its wiping and its final weighing was about 4 minutes. The water-absorption tube had a tendency to pick up weight over an indefinite period of time, especially if any static charge was present. With constant temperature and relative humidity about 45 per cent the increase over a 2-minute period at the time of weighing was between the limits 0.000 and 0.005 mg. The ascarite tube was exceptionally constant if there was no static charge present; the increase in weight over a 2-minute period at the time of weighing was between the limits 0.000 to 0.003 mg. With constant temperature and humidity above 45 per cent and no static charge on the tube the weight was constant for as long as 5 minutes. It has been found that consecutive weighings taken at the exact time interval during each routine analysis have given analytical results which check well within the limits of accuracy as shown by Table I. About 10 minutes' time for each analysis has been saved, which has been found to be an important item in routine analysis.

Cleaning and Wiping

The method of cleaning and wiping the tubes has been modified to make the above weighing system possible. The absorption unit was removed from the combustion train and 50 cc. of air were pulled through it to remove the oxygen, as described by Niederl and Roth (12). After washing the hands in cold water, the separate absorption tubes were wiped from end to end with a freshly washed flannel from which a few drops of water could still be squeezed. The tube was immediately wiped by the first set of soft chamois skins with a very few soft strokes, until the chamois glided smoothly over the surface. All strokes had to be partly rotatory and from the center toward the ends only, never in the reverse direction. The open ends of the tube were then cleaned with a tuft of cotton on a wire, and this treatment was followed by a second wiping with a second set of chamois, when even more gentle treatment had to be given in order to prevent the formation of static charges.

Following this wiping it was found that any foreign materials remaining on the glass surface could be easily seen by viewing the tube against a narrow beam of light from a dark background. For this purpose a simple apparatus was constructed as follows: A 60-watt incandescent bulb as a source of light was placed in a tin box 12.5 × 15 × 12.5 cm. (5 by 6 by 5 inches). The front of the box contained an opening on which a ground-glass panel was mounted. The glass panel was entirely covered by a dull black opaque paper, except for a slit 2 mm. wide by 12 cm. long and a second opening about 2.5 cm. (1 inch) lower, which was masked from view

by an upturned hood of black paper so that light was thrown up on the tube while the source was hidden from the eye. This box was fastened on the wall, with the light opening in a horizontal direction.

In the final wiping, the tube was held up within a few centimeters of the slit, so that the operator could not see the light directly. Any lint, fiber, or dirt which might still be clinging to the tube appeared in sharp relief against the black background, as the light from the opening passed over the top surface of the tube. Every piece of foreign material of any weighable size was easily seen and removed, so that this source of error was definitely removed. Rewiping and reweighing of tubes were found to be superfluous after this treatment. As an added precaution, the tube was stroked with a camel's-hair brush before being placed in the balance, special care being given to the tip end which was last touched with chamois.

Elimination of Static Charge

In this laboratory the author has had a great deal of trouble with static charge on the surface of the tubes, which has been found to grow progressively worse as the relative humidity decreased. Hernler (9) reported better results at high relative humidity than low, but did not mention static charge. In this laboratory, above a relative humidity of 45 per cent little static was noticed, but below 40 per cent the static charge became severe. The charge was frequently so great that even with care in wiping and discharging, the pan of a Kuhlmann balance was rotated on its axis by the approach of the absorption tube to be weighed. The weighing in this case, needless to say, was so disturbed that the first reading was often in error by as much as 1 mg., the observed weight being less than the true weight in general. At the end of a 15-minute wait this static charge was usually dissipated and a fairly accurate weighing obtained, but since the weighing was desired at the completion of wiping, it was necessary to prevent static charges.

A charged tube was detected in two ways. If a tube surface was charged the lint or fibers would stand perpendicular to the surface of the tube. This phenomenon was especially noticeable with the above-mentioned apparatus for viewing the absorption tubes. The second test for static charge consisted in bringing the tube up to a pith ball suspended on a silk string about 15 cm. (6 inches) long. If there was a heavy charge on the tube, the pith ball would swing through an arc of 5 or 6 cm. (2 or 3 inches) to contact the absorption tube, although occasionally the charge would be repulsive. This charge was especially noticeable on the surface of glass which covered the dry magnesium perchlorate, but was also heavy at the tips of the tube.

The first method of eliminating static charges studied, involved their removal from the surface of the tube. The balance, as well as the rack on which the tubes rest before weighing, was grounded. Uranium acetate and various radioactive ores were placed in the balance case, but none gave any material dissipation of the charge on the tubes. The static could be discharged by touching the tube in several positions with the fingers, if the charge was only slight, but a heavy charge could never be removed in this manner.

Another procedure to ensure a tube free from charge was to prevent its being built up on the glass surface. This was accomplished by wiping as previously outlined, with the added precaution of using chamois that had been kept in a covered dish on a rack above a shallow layer of water. In extremely bad cases of static charge the chamois were moistened in a blast of steam before using, so that they felt slightly moist. A careful wiping with these chamois gave a clean tube that was free of static.

A daily record of the relative humidity and degree of static trouble showed vividly that the lack of moisture in the air was primarily responsible for this static trouble. With cold clear winter weather the relative humidity was often below 40 per cent which was the lowest relative humidity at which static charges were absent. A successful method of static elimination was found to consist simply in keeping the atmosphere in the room at or above 45 per cent relative humidity, by allowing a flow of steam from a steam bath to raise the moisture content of the room to a relative humidity of 45 per cent or above. A steam valve permitted ample adjustment to keep the humidity quite constant.

TABLE I. RESULTS OF 54 ANALYSES TAKEN FROM THREE PAPERS (1, 3, 15)

Average Deviation from Theory		Average Deviation in Checks		Tendency	
C	H	C	H	C	H
0.125	0.123	0.099	0.144 ^a	+0.06	-0.01

^a Would have been 0.126 if one widely divergent check had been omitted where the results were on both sides of theory.

The analyses of Table I were made over a period comprising every season of the year. From these and other data compiled in this laboratory it has been found that there is no appreciable seasonal variation except when the static is not properly taken care of in the winter, when results tend to be high. That the high humidity found in the summer months has not affected the weighings in any manner, speaks well for the elimination of the rest of the absorption tubes beside the balance for the standard 15 minutes.

Summary

A method of handling and weighing absorption tubes has been developed which includes the following features: (1) location of the balance in a room kept at a fairly constant temperature and where sudden changes in temperature were never observed; (2) use of Pregl absorption tubes, since they are the simplest tubes to clean; (3) weighing tubes immediately after wiping to eliminate the necessity of closing the ends of the tubes; (4) saving about 10 minutes on each analysis; (5) use of a special background for viewing absorption tubes during cleaning; and (6) elimination of static charge on the glass surface, by proper wiping and, still more important, by maintaining the relative humidity of the laboratory at or above 45 per cent.

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Determination of Elementary Sulfur in Gasoline and Naphtha

A Quantitative Method

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THE presence of excessive free or elementary sulfur in gasoline or naphtha has been avoided for many years. The corrosion of the metal parts of automobiles (2, 10), particularly copper and its alloys, has been attributed to the effect of this component. A recent study (3) of color stability of gasoline has shown the influence of elementary sulfur upon this property. Sulfur may be present, normally, through oxidation of hydrogen sulfide to sulfur, or addition of sulfur in the doctor, or sodium-plumbite, sweetening process. Since hydrogen sulfide is usually removed from gasolines before much oxidation has occurred, the latter source accounts for the greater proportion. In the sweetening process, the elementary sulfur is added during the treatment of the gasoline with doctor solution to convert the malodorous mercaptans to disulfides. In order to assure rapid settling of the lead sulfide formed in the reaction, an excess of sulfur must be used.

A careful control of the sulfur addition must be exercised to avoid a corrosive gasoline. The criterion in specifications of a corrosive gasoline is based upon the results of a copper-strip test, A. S. T. M. Designation D130-27T. This test usually requires 3 hours for completion and the result is only qualitative. In most gasolines the amount of excess elementary sulfur that is required to give a corrosive copper-strip test is between 0.003 and 0.004 per cent by weight.

There have been many methods (4-9, 11-13) recommended for the quantitative determination of elementary sulfur in gasoline. Most of these are long or too involved to be satisfactorily used in a refinery doctor treating plant. Time is the essence of most refinery operations and a rapid determination is extremely advantageous. Mercury is often used as a quick method for the detection or estimation of elementary sulfur. It is sensitive to extremely small quantities which are much lower than the amounts required for a corrosive copper strip. A quantitative determination of the precipitated mercury sulfide involves a long and tedious analytical procedure. In addition, mercury reacts with organic peroxides in cracked gasolines with the formation of a black precipitate similar in appearance to mercury sulfide.

The method proposed in this paper allows a rapid quantitative determination of elementary sulfur which involves a simple laboratory technic readily usable by the small refiner. It is particularly applicable to a ready control of the doctor sweetening process and it may in time serve as a substitute for the copper-strip test in gasoline specifications.

In the determination a known quantity of a mercaptan is added to the gasoline. The mixture is agitated with doctor solution until complete reaction of the sulfur and the added mercaptan has occurred. Since the excess mercaptan is now present as lead mercaptide, it is restored to the original mercaptan by dilute sulfuric acid. Following a wash with acidified cadmium chloride solution to remove the liberated hydrogen sulfide, the gasoline is titrated with silver nitrate solution (1) to determine the excess mercaptan. The used mercaptan, obtained by difference, permits a calculation of the free sulfur content of the original gasoline. The method is not applicable to oils heavier than kerosene because of the difficulties involved in the determination of their mercaptan sulfur contents.

Reagents

The only special reagent required for the determination is a standard butyl mercaptan solution in a cleaners' naphtha. The preferred butyl mercaptan is of the chemically pure Merck grade, boiling point 98° C. and free of elementary sulfur. The cleaners' naphtha must not contain any mercaptans or elementary sulfur. The former may be removed by precipitation by agitation with a silver nitrate solution. By agitation of the naphtha with mercury, the elementary sulfur may be precipitated as mercury sulfide which may be readily removed by filtration. The standard (0.5 M) solution of the mercaptan is prepared by the addition of 45.07 grams of butyl mercaptan in sufficient of the cleaners' naphtha to obtain 1 liter of the solution. The solution should be retained in a tightly stoppered dark bottle to avoid deterioration. The remaining reagents are common to the usual petroleum laboratory and consist of a 30° Bé. sodium plumbite solution, sulfuric acid (20 per cent concentration), and cadmium chloride solution (10 per cent, containing 1 cc. per 100 cc. solution of concentrated hydrochloric acid). The reagents used in the mercaptan titration (1) are 0.05 N silver nitrate, 0.05 N ammonium thiocyanate, and ferric alum indicator.

Procedure

Add by means of a buret exactly 3 cc. of the standard butyl mercaptan solution to 147 cc. of the gasoline to be tested. Agitate thoroughly in a small separatory funnel for 5 minutes with 20 cc. of the sodium plumbite solution. Allow to settle and drain the plumbite. Wash the oil by agitation with 50 per cent by volume of 20 per cent sulfuric acid until all the black lead sulfide is dissolved and the oil is restored approximately to its original color. Settle and withdraw the acid. Wash the oil by agitation with 50 cc. of a 10 per cent solution of acidified cadmium chloride to remove the hydrogen sulfide. Remove the cadmium chloride solution by drainage. Determine the mercaptan sulfur content on 100 cc. of the residual oil (1) by agitating the gasoline with an excess of silver nitrate solution and back-titrating with ammonium thiocyanate using ferric alum as an indicator. Express

TABLE I. MIDCONTINENT STRAIGHT-RUN GASOLINE

Weight of Elementary Sulfur		Elementary Sulfur		Error %
Present	Found	Present	Found	
Gram	Gram	%	%	
0.015	0.0164	0.02	0.0218	+0.0018
0.01125	0.01042	0.015	0.0139	-0.0011
0.0075	0.00733	0.01	0.0098	-0.0002
0.00562	0.00559	0.0075	0.00745	-0.00005
0.0045	0.00458	0.006	0.0061	+0.0001
0.00375	0.00374	0.005	0.00499	-0.00001
0.0030	0.0028	0.004	0.00373	-0.00027
0.001875	0.00198	0.0025	0.00264	+0.00012
0.001125	0.00129	0.0015	0.00172	+0.00022

TABLE II. MIDCONTINENT CRACKED GASOLINE

Weight of Elementary Sulfur		Elementary Sulfur		Error %
Present	Found	Present	Found	
Gram	Gram	%	%	
0.015	0.0168	0.02	0.0224	+0.0024
0.01125	0.01158	0.015	0.0154	+0.0004
0.0075	0.0073	0.01	0.0097	-0.0003
0.00562	0.00561	0.0075	0.00748	-0.00002
0.0045	0.0044	0.006	0.00586	-0.00014
0.00375	0.00399	0.005	0.00532	+0.00032
0.0030	0.00299	0.004	0.00399	-0.00001
0.001875	0.00198	0.0025	0.00264	+0.00014
0.001125	0.00132	0.0015	0.00176	+0.00026

TABLE III. MIDCONTINENT STRAIGHT-RUN GASOLINE	
Per Cent by Weight of Elementary Sulfur	Corrosion Test
0.025	Positive
0.0125	Positive
0.00625	Positive
0.004	Questionable
0.003125	Negative
0.0015625	Negative
0.00078125	Negative

TABLE IV. MIDCONTINENT CRACKED GASOLINE	
Per Cent by Weight of Elementary Sulfur	Corrosion Test
0.025	Positive
0.0125	Positive
0.00625	Positive
0.004	Questionable
0.003125	Negative
0.0015625	Negative
0.00078125	Negative

the mercaptan sulfur content of the residual oil in grams of sulfur per 100 cc. of gasoline, which is equal to cubic centimeters of silver nitrate solution multiplied by its normality and the conversion factor of 0.032.

By using 100 cc. for the titration and calculating the mercaptan content in terms of grams of sulfur, the following calculations are simplified. The elementary sulfur content of 100 cc. of the gasoline is calculated by means of the following formula:

$$X = \frac{1/2 \text{ mol. wt. of sulfur} \times \text{grams of butyl mercaptan used}}{\text{mol. wt. of butyl mercaptan}}$$
where X = grams of sulfur in 100 cc. of the sample, and grams of butyl mercaptan used = grams of butyl mercaptan added - grams of mercaptan sulfur in 100 cc. of residual oil $\times \frac{\text{mol. wt. of butyl mercaptan}}{\text{mol. wt. of sulfur}}$

Experimental

In the experimental study of this procedure several synthetic mixtures of known elementary sulfur contents were prepared. Concentrated stock solutions of elementary sulfur in midcontinent straight-run and cracked gasolines were made. Elementary sulfur and mercaptans were removed from each of these solvents by mercury and silver nitrate, respectively, before use. The stock solutions were used in the preparation of a sample of any desired percentage of elementary sulfur by suitable dilution with the proper solvent. Determinations were made on each of these prepared samples, and the results are shown in Tables I and II.

The results indicate that the proposed method gives an accurate quantitative determination of elementary sulfur in cracked and straight-run gasolines. The method is suitable as a control of the addition of elementary sulfur during the sweetening process, since the accuracy in the concentration range of a corrosive copper strip is satisfactory.

Investigation of the Determination

ELEMENTARY SULFUR REQUIREMENT FOR A CORROSIVE COPPER-STRIP TEST. The stock solutions of elementary sulfur in cracked and straight-run gasolines were properly diluted to extend over the desired range of sulfur contents. Copper-strip corrosion tests, A. S. T. M. Designation D130-27T, were made on each prepared sample. The results of these tests are shown in Tables III and IV.

In each of these two gasolines, an elementary sulfur content of approximately 0.004 per cent by weight was required to obtain a corrosive copper-strip test. From the authors' experience, the amount may show a slight variation with different gasolines, although this is probably partially a function of the accuracy of the test method.

USE OF SULFURIC ACID TO CONVERT LEAD MERCAPTIDE. The concentrated butyl mercaptan solution was diluted with sufficient sulfur-free gasoline to prepare solutions containing several percentages of mercaptan. Each of these samples was shaken with plumbite until all the mercaptan was converted to lead mercaptide. The plumbite solution was separated by drainage and the gasoline was washed with 20 per cent sulfuric acid until all the yellow color had disappeared, indicating that no lead mercaptide remained. A mercaptan titration was made on the residual oil to determine the loss of butyl mercaptan, if any. A comparison of the mercaptan content found after this treatment with that present in the original solution is shown in Table V.

Based upon this comparison, no butyl mercaptan is lost by this treatment with plumbite and sulfuric acid solutions. The mercaptan sulfur contents of the gasolines after treatment check the actual values of the original solutions well within the accuracy of the titration.

EFFECT OF HYDROGEN SULFIDE. In the presence of elementary sulfur, lead mercaptides are converted into disulfides with the formation of lead sulfide. The addition of dilute sulfuric acid results in the formation of hydrogen sulfide. The removal of this gas is necessary to permit a satisfactory mercaptan titration for the determination of the unused butyl mercaptan. Several gasolines of known mercaptan contents determined by titration were agitated with plumbite solution. The plumbite was properly drained and a small amount of powdered lead sulfide added to each gasoline. These mixtures were shaken with a 20 per cent sulfuric acid solution until the lead sulfide was converted to lead sulfate. The acid was drained and each sample of oil was washed with a cadmium chloride solution to remove the hydrogen sulfide. A mercaptan titration was conducted on each of the residual oils and compared to a similar determination on each original gasoline as shown in Table VI. The results show that the hydrogen sulfide may be removed with the acidified cadmium chloride solution without any effect on the mercaptan content of the gasoline.

TABLE V. MERCAPTAN SULFUR	
Mercaptan Sulfur Added %	Mercaptan Sulfur Found %
0.246	0.240
0.129	0.127
0.060	0.059
0.031	0.030
0.0163	0.0161
0.0082	0.0081

TABLE VI. MERCAPTAN SULFUR	
Mercaptan Sulfur in Original Gasoline %	Mercaptan Sulfur in Residual Oil %
0.072	0.070
0.0528	0.0523
0.018	0.0178
0.015	0.0147
0.005	0.0047

TABLE VII. MERCAPTAN SULFUR	
Mercaptan Sulfur in Original Gasoline %	Mercaptan Sulfur in Residual Oil %
0.083	0.081
0.060	0.058
0.021	0.020
0.01	0.009
0.005	0.004

INFLUENCE OF THE PRESENCE OF DISULFIDES. Since butyl disulfide is formed in the elementary sulfur determination, the effect of its presence on the mercaptan titration was determined. Normal butyl disulfide (0.10 per cent by weight) was added to several unsweetened gasolines of known mercaptan contents. These gasolines were agitated with plum-

bite and settled, and the plumbite was drained. They were then agitated with dilute sulfuric acid, and the oil was separated and titrated for mercaptan content with silver nitrate. Table VII shows a comparison of the mercaptan contents of the original gasolines, free of disulfides and elementary sulfur, with those obtained on the treated oils. These mercaptan contents check each other satisfactorily. The presence of disulfides has no effect on the determination.

OTHER APPLICATIONS. This method may be used to determine quantitatively the theoretical amount of sulfur required to sweeten a gasoline. The same procedure is followed with the exception of using the sour gasoline and without the addition of a known quantity of butyl mercaptan. The unsweetened gasoline is agitated with plumbite, settled, and the plumbite drained. The gasoline is treated with dilute sulfuric acid, separated, and washed with cadmium chloride solution. The residual oil is titrated with silver nitrate for mercaptan sulfur content. The remaining mercaptans are a measure of the additional sulfur required which is calculated by the following equations:

$$\% \text{ of mercaptan sulfur} = \frac{\text{cc. of silver nitrate} \times \text{normality} \times 0.032}{\text{wt. of sample}}$$

$$\% \text{ of sulfur required} = \frac{\% \text{ of mercaptan sulfur in residual oil}}{2}$$

The actual amount of sulfur required will be greater than the determined theoretical value by an amount necessary to give a sharp break of the lead sulfide from the gasoline. This amount should not be allowed to exceed the quantity which will cause a corrosive copper-strip test. A knowledge of the

theoretical requirement will aid in preventing the refiner from using excessive sulfur.

Conclusions

The proposed method is a rapid, accurate quantitative determination of the elementary sulfur content of gasoline. The method facilitates the testing and control of gasolines or copper-strip corrosion during refinery sweetening operations by minimizing the time required for the determination. The test can be readily completed in 0.5 to 0.75 hour.

The proposed method may be used to determine the theoretical quantity of elementary sulfur required in the sweetening of a gasoline. By this means the addition of excessive sulfur over the amount necessary for a satisfactory break may be avoided.

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A System for the Qualitative Analysis of the Alkaline Earth and Alkali Groups

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ALTHOUGH the procedures recommended by Noyes (3) and Bray (2) for detecting the alkaline earth and alkali metals for the most part give accurate results with careful handling, it is found in practice that some of the filtrations are time-consuming. It is the purpose of this paper to describe a system which is more convenient and rapid and which also gives accurate results. All the separations in the two groups have been tested carefully and where it has not been found possible to make improvements, as in the separation and detection of barium and strontium, the methods employed by Noyes and Bray have been adopted.

The new system has been used with success for two years by a class in qualitative analysis in Harvard College. The number of errors made by students in identifying the ions of these groups has been decidedly smaller than it was previously with other systems. With the new procedures the precipitates which must be filtered in order to separate ions or groups of ions are of such a nature as to promote rapid filtration and to give clear filtrates. Prompt and decisive results are obtained in the final tests even when only traces of the ions are present.

In this system advantage is taken of the fact that neither the very delicate *p*-hydroxybenzene-azoresorcinol test for magnesium described by Suitsu and Okuma (7) nor the magnesium uranyl acetate test for sodium described by Blanchetière (1) is interfered with by traces of the alkaline earth metals. The convenient process recommended by Rawson (5) for the quantitative separation of barium and strontium from calcium is employed.

The detection of small quantities of calcium in the presence of much magnesium proved to be a difficult problem, particularly when strontium was also present. It was finally solved by evaporating the solution of calcium and magnesium nitrates in nitric acid to dryness and igniting the residue. The magnesium was thus rendered sufficiently insoluble so that when the calcium was extracted with water a delicate test for it could be made with potassium oxalate. With much magnesium in the solution the oxalate test for calcium is both insensitive and unreliable.

Materials and Reagents

In general, solutions and reagents were prepared from reagent-grade chemicals. It was necessary, however, to purify calcium nitrate and magnesium nitrate by repeated recrystallization.

Magnesium uranyl acetate reagent was made up according to the directions of Noyes and Bray (4). The magnesium reagent was prepared according to the directions of Ruigh (6). Other reagents were prepared according to Noyes' directions (3).

Procedure

Prepare a solution free from members of the other groups and containing approximately 45 milliequivalents of ammonium salts and not more than 500 mg. of the elements of the two groups in 25 ml. Heat to boiling, add 10 ml. of ammonium carbonate reagent, and keep at the boiling point for 3 minutes. A white precipitate indicates the presence of calcium, strontium, barium, or more than 50 mg. of magnesium. Filter off the precipitate, wash with hot water, and test for these elements.

Next evaporate the filtrate to dryness and ignite to expel ammonium salts. Extract the residue with 5 ml. of concentrated hydrochloric acid, warming gently and rubbing with a glass rod. After cooling completely, decant the acid and evaporate to dryness. Dissolve any residue, indicating the presence of sodium, potassium, or magnesium, in 3 ml. of water. To 1 ml. of the solution, which is filtered if it is not perfectly clear, add a small drop (0.02 ml.) of *p*-nitrobenzene-azoresorcinol reagent followed by a drop of sodium hydroxide. A sky-blue precipitate indicates the presence of magnesium. To a second milliliter add 1 ml. of sodium cobaltinitrite reagent. A yellow precipitate indicates the presence of potassium. Dilute the remaining milliliter of solution with 19 ml. of water, and test 1 ml. of this dilute solution for sodium by adding 0.5 ml. of alcohol and 1 ml. of magnesium uranyl acetate reagent. A fine granular yellow precipitate indicates the presence of sodium.

If the unknown contains phosphate at this point it must be removed before proceeding with the sodium test, as it will produce a flocculent precipitate of uranyl phosphate. This may be done by diluting the 1 ml. of solution with 5 ml. of water and adding 5 ml. of magnesium ammonium nitrate reagent and 5 ml. of ammonia. Heating to boiling hastens the complete precipitation of the phosphate. Filter off the precipitate, evaporate the filtrate to dryness, and ignite to remove ammonium salts. Then extract the magnesium residue with 20 ml. of water and proceed with the test for sodium.

To separate barium and strontium from calcium and any large quantity of magnesium which may be present, dissolve the precipitated carbonates in 2 *N* nitric acid and evaporate the solution just to dryness. After cooling, treat the dry nitrates with 5 to 10 ml. of concentrated nitric acid (specific gravity 1.4). An insoluble residue indicates the presence of barium or strontium. Ten minutes are usually ample for the solution of calcium and magnesium nitrates which may be present, although if the nitrate residue has been overheated basic magnesium nitrate dissolves slowly. Filter off the barium and strontium nitrates on an asbestos filter, wash with 5 ml. of concentrated nitric acid, and then dissolve by pouring 10 ml. of water through the filter. The solution after neutralizing with ammonia may be analyzed for barium and strontium according to Noyes (3), beginning with the second paragraph of procedure 72 and ending with procedure 75.

Evaporate the filtrate of concentrated nitric acid, containing calcium and frequently considerable quantities of magnesium, to dryness in a Pyrex beaker. If magnesium is present, ignite the residue of nitrates as strongly as possible with two Bunsen burners. The evolution of red-brown fumes of nitrogen dioxide indicates the presence of much magnesium, and ignition should be continued until these fumes are no longer given off. Since the glass is attacked, this ignition must be carried out in a container free from calcium, such as a Pyrex beaker. After cooling the residue, treat with 10 ml. of freshly boiled water and heat almost to the boiling point for 10 minutes. Filter the solution from the insoluble magnesium oxide and any undissolved calcium oxide, and test for calcium by the addition of 1 ml. of potassium oxalate solution. If magnesium is not present, dissolve the nitrate residue in water, make alkaline with ammonia, and test for calcium with potassium oxalate.

Notes on Procedures

Tests indicate that in general it is possible to find 1 mg. of any element in the two groups in the presence of 500 mg. of any other element of the groups. It was thought advisable in the case of magnesium, however, to select 250 mg. as the maximum amount which may be present in an analysis. Because of the small equivalent weight of the element, this limit is likely to be exceeded only in the analysis of magnesium alloys or magnesium oxide.

The most serious objection to this system is that as much as 3 mg. of barium or 2 mg. of strontium when present alone may escape precipitation by ammonium carbonate under the conditions described. However, if a large amount of one of the elements of the alkaline earth group is present, traces of the others are co-precipitated as carbonates to an extent sufficient to ensure their detection. Consequently, if no precipitate results when the ammonium carbonate reagent is added and if it is desired to detect traces of barium and strontium, the solution should be evaporated to as small a volume as suffices to keep ammonium salts in solution. A drop of sulfuric acid is then added and the solution allowed to

stand for several hours. If a trace of barium or strontium sulfate separates, it may be identified most easily by a flame test. This test will detect 1 mg. of barium with certainty, but the precipitation of traces of strontium by sulfate is very slow and uncertain.

The separation of barium and strontium from calcium and magnesium, which is the chief innovation of this procedure, was tested thoroughly. It was found that 1 mg. of barium or strontium could be found easily in 500 mg. of calcium when the dried nitrates were treated with 10 ml. of concentrated nitric acid. This amount of the concentrated acid also serves to dissolve completely 250 mg. of magnesium if sufficient time is allowed. The presence of either calcium or magnesium appears to increase the sensitivity of the test for barium or strontium, for these insoluble nitrates are left in a finely divided form when the soluble nitrates are extracted. It was also found that, of 1 mg. of calcium, enough to give a decided test was extracted from 500 mg. of either barium or strontium when the nitrates of these elements were treated with 10 ml. of concentrated acid.

In a series of experiments designed to find how serious the effect of slight dilution of the concentrated nitric acid might be, solutions containing 400 mg. of calcium with varying quantities of barium and strontium as the nitrates were evaporated to dryness and treated with 10-ml. portions of nitric acid of varying concentration. The results of these experiments are presented in Table I.

TABLE I. EFFECT OF DILUTION UPON THE SENSITIVENESS OF THE CONCENTRATED NITRIC ACID TEST FOR BARIUM AND STRONTIUM IN CALCIUM

In 400 Mg. of Ca Ba Mg.	Sr Mg.	Specific Gravity of HNO ₃		
		1.40	1.36	1.31
1	—	+	—	—
2	—	0	+	—
3	—	0	0	+
5	—	0	+	+
10	—	0	0	+
—	1	+	—	0
—	2	+	—	0
—	3	0	?	0
—	5	0	+	—
—	10	0	0	—
—	15	0	0	+

+ = Residue noted, positive test.
 — = Complete solution, negative test.
 0 = No experiment.
 ? = Uncertain.

Since the dilution from acid of specific gravity 1.40 to specific gravity 1.36 involves the addition of 25 ml. of water to 100 ml. of the concentrated acid, it is evident that any slight dilution due to water retained by the alkaline earth nitrates after evaporation to dryness will not seriously impair the sensitiveness of the test.

The solubilities of barium and strontium nitrates in nitric acid of various concentrations are now being measured in this laboratory in order to supplement qualitative data of Table I. It is surprising that this convenient and sensitive test is not more widely employed.

Since the presence of too much potassium results in the precipitation of needle-like crystals when magnesium (or zinc) uranyl acetate is employed to test for sodium, it is necessary to adjust carefully the concentrations of the solutions being tested and of the reagents in order to prevent interference. The conditions described in the procedure are chosen to avoid the use of a large quantity of the expensive reagent while permitting adequate delicacy for sodium without danger of interference by potassium.

Since the chief objection to Noyes' method of precipitating strontium as the chromate in basic solution by the addition of alcohol is the difficulty of obtaining a clear filtrate sufficiently

free from the very fine precipitate to permit a test for calcium, it was decided to employ it, for in the present system the calcium has already been removed and it is necessary only to collect enough of the strontium precipitate for a confirmatory test.

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Determination of Sodium in High Aluminous Material

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RECENTLY there has developed a need for the precise determination of sodium in aluminous materials of a refractory nature, such as calcined alumina. Past experience has shown that the well-known J. Lawrence Smith method may yield satisfactory results from the standpoint of accuracy and precision. This method, however, is open to criticism when used under practical laboratory conditions. It is tedious and time-consuming. Rather large corrections must be made in results for reagent blanks unless extremely pure reagents are available. Lamar, Hazel, and O'Leary point out that many special precautions must be taken (3).

Since the sodium uranyl zinc acetate method of Barber and Kolthoff (1) has made available a satisfactory procedure for the determination of sodium in solution as sulfate, the problem in the present case becomes one of decomposing the sample and converting the salts present to sulfates. According to Hillebrand and Lundell (2), Jannasch suggested ammonium fluoride as a satisfactory fusion reagent for some silicate minerals. Despite the absence of silicates from the aluminous materials to be analyzed, it was thought that if ammonium fluoride would render the sample amenable to solution in sulfuric acid, the sodium uranyl zinc acetate method would solve the remainder of the problem.

While ammonium fluoride or ammonium bifluoride in salt form can be used in this determination, the authors believe it is simpler to use hydrofluoric acid and form the ammonium compound *in situ* by the addition of ammonium hydroxide.

The sodium content is determined by reducing the equivalent uranium salt to a valence of 4 by means of a coil of aluminum wire and titrating to the valence of 6 by means of permanganate solution. The aluminum coil (Figure 1) is to be preferred to amalgamated zinc for two main reasons. Zinc is apt to carry the reduction of the uranium salt below the valence of 4, thus necessitating an oxidation back to that stage before titration is begun.



FIGURE 1. ALUMINUM COILS USED TO REDUCE URANIUM SALT

Aluminum does not carry the reduction below the valence of 4. When zinc is used it must be filtered off before the titration is made. The aluminum coil can be merely lifted from the solution. The coil of aluminum wire may be prepared by winding 150 cm. (5 feet) of 16- or 18-gage commercially pure aluminum wire around an appropriate form, such as a pencil.

The uranyl zinc acetate reagent used for precipitating the sodium is made up as follows:

- | | |
|---|--|
| A. Uranyl acetate, 10 grams
Acetic acid, 6 grams
Water to make 65 grams | B. Zinc acetate (3H ₂ O), 30 grams
Acetic acid, 30%, 3 grams
Water to make 65 grams |
|---|--|

After the salts in A and B are dissolved by warming, the solutions are mixed, a few milligrams of sodium chloride added, and the solution is allowed to stand 24 hours. The solution is filtered immediately before it is to be used. This procedure gives a clear solution of reagent saturated with sodium, and the precipitation is carried out with as little change in temperature as possible. If it is maintained at room temperature, satisfactory results will be obtained.

Procedure

To a large platinum dish add 1 gram of sample, 20 cc. of concentrated hydrofluoric acid, and 20 cc. of water. Then add 50 cc. of 1 to 1 ammonium hydroxide and evaporate to fumes. In the case of very refractory materials it may be necessary to repeat this operation two or three times. This necessity is exceptional and is not ordinarily encountered. Heat under a Dutch oven until almost dry but still moist and fuming. Add 5 cc. of concentrated sulfuric acid, and fume till all fumes are driven off. Ignite at dull red heat. Add 5 cc. of concentrated sulfuric acid and heat until all fumes are driven off. Add 2 cc. of concentrated sulfuric acid, and fume for a few minutes, but do not drive off all the acid. (Leave about 1.5 grams of sulfuric acid. This is the most important step in this procedure.)

Add 50 cc. of hot water, evaporate to 7 cc., cool, and add 70 cc. of the uranyl zinc acetate reagent. Let stand at least 0.5 hour and filter by suction through an 11-cm. filter, using a little paper pulp. Wash with the reagent just enough times to transfer all the precipitate from the beaker to the filter. Wash twice with 2-cc. portions of 95 per cent ethyl alcohol and five times with acetone. Remove excess acetone by means of suction. This can be speeded up a little by drying at 105° C. for a few minutes. Wash the suction flask carefully and use it to receive the sodium uranyl zinc acetate which is washed out of the filter with hot water. Transfer this solution to a 250-cc. beaker, add enough potassium permanganate to color the solution and 30 cc. of 1 to 1 sulfuric acid. Place an aluminum coil in beaker and boil for 30 minutes. When reduction is complete, cool, remove coil, rinse off with water, and titrate with standard permanganate. A blank must be carried through with the determinations.

$$1 \text{ cc. } 0.1 \text{ N KMnO}_4 = 0.000382 \text{ Na} \\ = 0.000515 \text{ Na}_2\text{O}$$

The method as outlined was applied to samples which had been analyzed by the J. Lawrence Smith method with the results shown in Table I.

TABLE I. DETERMINATION OF SODIUM

J. Lawrence Smith Method	Ammonium Fluoride Method	J. Lawrence Smith Method	Ammonium Fluoride Method
%	%	%	%
0.63	0.67	0.58	0.58
0.56	0.55	0.41	0.43
0.65	0.67	0.12	0.13
0.52	0.51	0.44	0.44
0.67	0.66	0.54	0.57
0.51	0.52	0.06	0.05
0.61	0.63	0.20	0.21
0.55	0.58	4.45	4.45
0.58	0.58		

The method, of course, is specific for sodium, while the Smith method covers total alkalies, but the absence of other

alkali metals from the material being analyzed answers this possible objection. Ordinarily the range of concentration of sodium to be met falls within the range of the data in the table, although the size of sample to be used should be such as to provide not more than 10 mg. of soda.

The ammonium fluoride method requires only about one-half as much time as does the J. Lawrence Smith method.

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Quantitative Separation and Determination of Aluminum and Zinc

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DOBBINS and Sanders (1) have shown that aluminum can be determined quantitatively on pure solutions by the formation of lithium aluminate, basing their work on that done previously by Prociv (3) and Hegrousky (2). Their method consists of adding an excess of lithium chloride to the solution of the pure aluminum salt, then making the solution alkaline to phenolphthalein with dilute ammonium hydroxide. The precipitate is washed, dried, and ignited, and the aluminum calculated from the formula $2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$. They stated that this method gives more concordant results than the ammonium hydroxide method for the determination of aluminum, that it can be used in any conditions in which the ammonium hydroxide method is applicable, and that it has been used on alums with excellent results, but made no reference to its use if other metals are present.

In some work on zinc alloys, where an accurate method of separating zinc and aluminum was desired, the lithium aluminate method suggested a possible means of separation. The effect of ammonium salts (chloride, acetate, and tartrate) on the formation of lithium aluminate, in the presence of zinc, was studied and a separation attempted.

Reagents

Standard aluminum nitrate solution: 110 grams of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in distilled water and made up to 100 cc. This solution was standardized by pipetting out 25 cc., evaporating to dryness, igniting, and weighing the resulting aluminum oxide.
Standard zinc sulfate solution: 32 grams of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ dissolved in distilled water, made up to 100 cc., and standardized by pipetting out 25 cc., precipitating ZnNH_4PO_4 , igniting, and weighing as $\text{Zn}_3\text{P}_2\text{O}_7$.
A 10 per cent lithium chloride solution was made by dissolving 100 grams of lithium chloride in distilled water and making up to 1000 cc.
A dilute solution of ammonium hydroxide, approximately 1 N, was used, since it is easier to secure the alkalinity desired by addition of dilute solution dropwise.
Solid ammonium acetate was used.
Phenolphthalein was used as indicator. A very faint pink gives the desired alkalinity.
Wash solution: a 2 per cent solution of ammonium acetate.
Dilute nitric acid (1 to 6) was used.
Ammonium phosphate: a 20 per cent solution of $(\text{NH}_4)_2\text{HPO}_4$.

Procedure

Aliquot portions of the aluminum salt solution and zinc salt solution were pipetted out into a beaker and the volume was made up to 100 cc. Lithium chloride solution in excess of that required to precipitate lithium aluminate, a few drops of phenolphthalein, and 5 grams of solid ammonium acetate were added. Dilute ammonium hydroxide was then added drop by drop with constant stirring until a very faint pink color was obtained. The voluminous flocculent precipitate which formed was allowed to settle 10 minutes, then filtered and washed with a 2 per cent solution of ammonium acetate. An 11-cm. Whatman No. 40 filter paper was used. After washing, the filtrate was set aside for the determination of zinc, and the precipitate was dissolved off the paper in the smallest possible amount of hot dilute nitric acid into the beaker used in the original precipitation. The paper (still on the funnel) was washed with dilute nitric acid and finally a hole was punched in the bottom of the cone to ensure washing all the precipitate into the beaker. Five grams of ammonium acetate, 3 cc. of lithium chloride solution, and a few drops of phenolphthalein indicator were added and dilute ammonium hydroxide was then added dropwise with stirring until a faint pink color appeared. The lithium aluminate was allowed to settle, and was filtered and washed with 2 per cent ammonium acetate as before. The filtrate was added to that from the first precipitation and reserved for the determination of zinc. After a second reprecipitation was carried out in the same manner, the precipitate of lithium aluminate was filtered and washed with 2 per cent ammonium acetate, and finally with distilled water; then dried and ignited to constant weight at 900° to 950° C. The aluminum was calculated from the formula $2\text{Li}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$, which contains 47.40 per cent of aluminum.
The combined filtrate from the three precipitations was evaporated to 200 cc. and the zinc determined by the classic phosphate method.

TABLE I. EXPERIMENTAL RESULTS

Sample No.	Al Taken Gram	Al Recovered Gram	Zn Taken Gram	Zn Recovered Gram
1	0.0399	0.0401	0.0403	0.0400
2	0.0399	0.0400	0.0403	0.0402
3	0.0399	0.0401	0.0403	0.0404
4	0.0399	0.0401	0.0403	0.0402
5	0.0399	0.0403	0.0403	0.0396
6	0.0399	0.0391	0.0403	0.0404
7	0.0399	0.0405	0.0403	0.0404
8	0.0399	0.0397	0.0403	0.0403
9	0.0399	0.0400	0.0403	0.0408
10	0.0558	0.0558	0.0403	0.0411
11	0.0558	0.0559	0.0403	0.0402
12	0.0558	0.0555	0.0403	0.0406
13	0.0159	0.0155	0.0403	0.0401
14	0.0159	0.0155	0.0403	0.0401
15	0.0159	0.0157	0.0403	0.0403

Discussion of Results

The lithium aluminate method for the determination of aluminum in solution of pure aluminum salts was found to give better results than either the ammonium hydroxide or phosphate method. This is in accordance with the results of Dobbins and Sanders.

Several ammonium salts were used to prevent the precipitation of zinc under the same conditions in which lithium aluminate is precipitated: (1) Ammonium acetate does not interfere with the precipitation of lithium aluminate, and prevents the precipitation of zinc under the same conditions. (2) Ammonium chloride does not interfere with the precipitation of lithium aluminate and prevents the quantitative precipitation of zinc. (3) Ammonium tartrate prevents precipitation of both aluminum and zinc.

The voluminous precipitate of lithium aluminate mechanically traps some of the zinc. This difficulty is eliminated in this procedure by reprecipitating the aluminum. Reprecipitation releases the zinc and allows it to pass on into the filtrate.

A precipitate of more than 0.1 gram is too bulky to handle, and the aliquot portion should be chosen so as to give a pre-

cipitate of the aluminate not exceeding 0.1 gram. The precipitate forms at once, and is easily filtered and washed. In this separation a 2 per cent solution of ammonium acetate is used as a wash solution in order to prevent the precipitation of zinc with the aluminum during the washing. After the final precipitation and washing distilled water is used to remove ammonium acetate from the precipitate.

Summary

Zinc and aluminum can be separated quantitatively by precipitating the aluminum as lithium aluminate from solutions containing ammonium acetate; the zinc remains in solution and may be determined in the filtrate by the phosphate method.

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RECEIVED June 23, 1936.

Determination of Manganese in Tungsten and Ferrotungsten

Mixed Perchloric and Phosphoric Acids as Solvent and Sodium Bismuthate or Potassium Periodate as Oxidizing Agents

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METALLIC tungsten, ferrotungsten, and tungsten steels are soluble completely with no precipitation of tungstic acid by treatment with mixed perchloric and phosphoric acids. The most rapid solubility occurs at a temperature of 200° to 215° C. The tungsten is held in solution probably as phosphotungstic acid. Most, if not all, of the silicon is dissolved but dehydrated silica if formed does no harm.

The determination of manganese in metallic tungsten and ferrotungsten is generally carried out following a fusion with sodium peroxide. An alternative procedure consists in dissolving the sample using hydrofluoric acid in a platinum dish followed by nitric acid to oxidize the iron and perchloric acid to volatilize excess hydrofluoric acid. These two procedures are more rapid than the method to be described. The first requires constant attention and the other involves the use of platinum dishes and hydrofluoric acid. Both may be preferred as routine methods because of their speed. By the method to be described a longer period of time is required to dissolve the sample, but no attention is required during this treatment and the use of platinum and the troublesome hydrofluoric acid is avoided.

Provided perchloric acid and phosphoric acid can be shown to have no interfering action during oxidation of manganese using either sodium bismuthate or potassium periodate, the present method for solution of ferrotungsten and tungsten metal in preparation for determining manganese has many advantages over either the fusion method or hydrofluoric acid treatment. In addition, the troublesome formation of insoluble tungstic acid is entirely avoided. This paper has for its object the study of the improved method of solution thus applied.

The present work is the fifth of a series of papers dealing with analyses using mixtures of other mineral acids with perchloric acid resulting from the valuable solvent and oxidation properties of such mixtures. Potassium ferricyanide as reference standard in evaluating titanous solutions was thus studied by Smith and Getz (2). The determination of chromium in chrome-tanned leather and the volumetric determination of iron in leather was developed by Smith and Sullivan (4, 5). The determination of chromium in stainless steel using mixed perchloric, phosphoric, and sulfuric acids was described by Smith and Smith (3). The determination of manganese in nitric acid solution following oxidation using bismuthate is well known and the same determination in the presence of phosphoric acid and sulfuric acid, as will be shown, requires but slight modification. The determination of manganese following oxidation to permanganic acid using potassium periodate was developed by Willard and Thompson (6). The general subject of mixed perchloric, sulfuric, and phosphoric acids and their applications in analysis was developed by Smith (1).

Samples for Analysis

Bureau of Standards ferrotungsten, No. 75: W, 75.2 per cent; Mn, 1.16 per cent.

British Chemical Standards, No. 202-2: W, 80.7 per cent; Mn, 0.55 per cent.

Union Carbide and Carbon sample (courtesy of H. E. Cunningham), works analysis: W, 79.79 per cent; Mn, 0.24 per cent.

Bureau of Standards sample No. 75 was the only one of this list in which a series of analysts cooperated in determining the value for manganese. The mean value, 1.16 per cent manganese, represented the average value by nine separate analysts. The minimum value given was 1.14 per cent and the maximum found was 1.19 per cent. The British Chemical Standard No. 202-2 is seen to show the highest tungsten

content, but the manganese value was given as the findings of but one analyst.

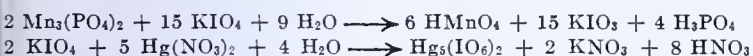
Solution of Tungsten and Ferrotungsten in Mixed Perchloric and Phosphoric Acids

Weigh into 500-ml. Erlenmeyer flasks 1-gram samples of ferrotungsten or tungsten metal in a finely divided condition. Provide each flask with refluxing heads such as that in A (Figure 1, 1), or the equivalent. Add 30 ml. of a mixture of 1 part of 72 per cent perchloric acid and 2 parts of 85 per cent sirupy phosphoric acid, and place flask and contents over a readily regulated burner and wire gauze. Heat gradually to 190° C. At 155° C. the acid mixture loses water and at 190° C. the solvent action begins in the case of ferrotungsten and the solution turns green with the precipitated tungsten scarcely attacked. Continue to heat to 200° to 215° C. and maintain at this temperature until all is in solution, which should be complete in 45 to 60 minutes with ferrotungsten and in a slightly longer time interval with tungsten metal. The reactions involved are omitted in the interests of brevity.

From this point the determination of manganese depends upon the choice of oxidizing agents employed. The silicon present is all or in part in solution as silicotungstic acid. Any not in solution does not interfere with subsequent operations.

Oxidation of Manganese Using Potassium Periodate

The solution of ferrotungsten or tungsten metal prepared as above described is cooled somewhat and diluted to 200 ml. with water. Add 0.3 gram of potassium periodate and heat to a gentle boil for 15 minutes to oxidize the manganese. Cool and add 4 to 5 grams of mercuric nitrate dissolved in water which precipitates the excess periodate (and iodate):



Filter the precipitated iodate and periodate through a Büchner funnel with asbestos filtering mat into a 500-ml. filtering flask containing an excess of standard ferrous sulfate. Wash the precipitate four times with water and titrate the excess ferrous sulfate with standard permanganate.

The amount of periodate used is sufficient to oxidize 15 mg. of manganese. Phosphoric acid being present aids in the oxidation of manganese and prevents interference from 1 to 1.5 mg. of chromium which is seldom present in tungsten or ferrotungsten. It is possible to oxidize twice as much manganese if 0.5 gram of periodate is used, but it is less convenient because of the bulk of mercuric salt to be filtered. By periodate oxidation of manganese the chlorine and possible traces of hydrochloric acid formed during the solution of the sample are either boiled off or oxidized to chlorine and evolved as such. Results of a series of analyses by this process are shown in Table I.

TABLE I. DETERMINATION OF MANGANESE IN FERROTUNGSTEN (B. of S. No. 75, 1.16% Mn. HMnO_4 filtered into 50.00 ml. of 0.0434 N FeSO_4 and excess of latter back-titrated using 0.0588 N KMnO_4)

Sample	0.0588 N KMnO_4 Required		Manganese Found		Error	
	Ml.	Mg.	%	Mg.	%	
0.8941	21.00	10.32	1.154	-0.05	-0.006	
1.2299	14.26	14.70	1.193	+0.44	+0.035	
0.9895	19.65	11.22	1.134	-0.25	-0.026	
0.8268	20.03	9.49	1.148	-0.10	-0.012	
			Av. 1.158	+0.01		

A series of six additional determinations not tabulated for the sake of brevity showed the following percentages of manganese found: 1.158, 1.144, 1.170, 1.157, 1.172, and 1.164, or an average of 1.161 per cent to compare with the certificate value of 1.16 per cent manganese.

Oxidation of Manganese Using Sodium Bismuthate

Dissolve the sample as above described, cool somewhat, and add 20 ml. of concentrated nitric acid. Boil gently until the chlorine and hydrochloric acid formed in the solution of the sample are decomposed or boiled off and the nitric acid has been evolved. Cool the contents of the flask by immersion in cold water and transfer the contents to a 400-ml. beaker. Reduce any violet color present, due to partially oxidized manganese, with a little ferrous sulfate solution. Add 15 ml. of concentrated sulfuric acid, bring to a boil, and add sodium bismuthate in small amount until the first definite pink color. Boil gently 5 minutes and reduce any pink or brown color with ferrous sulfate solution. Bring again to a gentle boiling temperature and add 1 gram of sodium bismuthate with stirring. Stir for a few minutes without additional heat and cool in a bath of cold water with continuous stirring.

Allow the oxidized solution and excess bismuthate to stand 10 minutes. Filter through an asbestos Gooch crucible into an excess of standard ferrous sulfate contained in a 500-ml. filter flask or its equivalent. Wash the precipitate left in the crucible with cold water and titrate the excess ferrous sulfate, using standard ceric sulfate and diphenylamine sulfonic acid as indicator to the first pink color which persists.

o-Phenanthroline indicator does not serve in this case because of the presence of tungsten. The use of permanganate in place of ceric sulfate does not give a definite end point, as is the case after periodate oxidation of manganese as previously described. Results of 14 consecutive analyses of B. of S. ferrotungsten No. 75 showed an average value of 1.155 per cent of manganese compared to the certificate value 1.16 per cent, and the values varied from 1.14 per cent to 1.18 per cent. Four consecutive determinations are recorded in Table II.

TABLE II. DETERMINATION OF MANGANESE IN FERROTUNGSTEN (B. of S. No. 75, 1.16% Mn. HMnO_4 filtered into 25.00 ml. of 0.05356 N FeSO_4)

Weight of Sample	0.02888 N Ceric Sulfate Required		Mn Found	Error
	Gram	Ml.	%	%
0.9227		12.88	1.152	-0.008
0.9634		11.12	1.161	+0.001
0.9541		11.05	1.174	+0.014
0.8952		13.10	1.179	+0.019

Av. 1.166

The ceric sulfate used in Table II was standardized using pure iron and B. of S. sodium oxalate, in the former case using *o*-phenanthroline as indicator, and in the latter case the potentiometric end point. The two values were found to be the same. The ferrous sulfate solution was then standardized against the ceric sulfate, using both a potentiometric and *o*-phenanthroline indicator system.

Seven consecutive determinations of manganese in sample No. 202-2 British Chemical Standards ferrotungsten were made using the bismuthate method. The average of these determinations was found to be 0.70 per cent. The variation in these results was from 0.68 to 0.73 per cent of manganese with one result of 0.77 per cent obviously in error.

Five consecutive determinations of manganese in the Union Carbide ferrotungsten, the works analysis for which showed 0.24 per cent of manganese, gave an average result of 0.183 per cent with a maximum range 0.175 to 0.191 per cent.

Literature Cited

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RECEIVED June 1, 1936:

Determination of Bismuth as Phosphate

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ALTHOUGH the gravimetric method for the determination of bismuth as phosphate has been in use since 1905, and a number of papers have been published regarding it, the details of procedure recommended show a wide range of variation, and there is a decided lack of detailed quantitative data upon which a rational procedure might be based. The data here reported are designed to supply this deficiency.

Properties of Bismuth Phosphate

The solubility of bismuth phosphate does not seem to have been determined. In order to ascertain its value a sample of the granular precipitate, separated from an acid solution, with a moderate excess of diammonium hydrogen phosphate was used. The well-washed precipitate was suspended in a large bottle of distilled water, which was kept immersed in a thermostat held at 27° C. and shaken occasionally, for a period of 15 days. Twenty 50-cc. portions of the solution were then evaporated in a platinum dish and the residue was heated to 140° C. Its weight was found to be 0.0033 gram, indicating a molal solubility less than that of barium sulfate. Assuming complete dissociation and no hydrolysis, this would correspond to a solubility product of approximately 1.1×10^{-10} . The residual precipitate showed no recognizable change in its physical properties and apparently had not undergone appreciable hydrolysis.

When caused to separate under the conditions defined below as standard, the precipitate consists of coarse granules, which settle almost at once and can be filtered and washed very rapidly. After drying at 240° C. the precipitate did not change in weight appreciably when heated to 1000° C.

When caused to separate from solutions containing large concentrations of ammonium phosphate, an appreciable amount of the latter seems to be adsorbed. The evidence for this statement is the fact that when such precipitates were dried up to a temperature of 240° C. the weight found was slightly in excess of the correct value and the precipitate was decidedly hygroscopic. After ignition to about 800° C. the excess of weight was eliminated and the precipitate was no longer hygroscopic.

In order to prevent the simultaneous separation of small amounts of basic salts it was found necessary that the solution should contain rather large concentrations of nitric acid and that both bismuth- and phosphate-containing solutions should be heated before mixing. Even under these conditions some of the precipitate which first separates is flocculent, but rapidly becomes granular at 80° C. This may be due in part at least to an aging effect, but is largely due to the presence of small amounts of basic salts, which change into the phosphate if the solution contains sufficient acid and if the temperature is kept at 80° C. The evidence for this statement is the fact that, with barely acid solutions and at ordinary temperature, the rate of change in the character of the precipitate is less, the tests for nitrate ion in the precipitate disappear more slowly, and the deficiency in the total weight of precipitate found, in solutions containing known amounts of bismuth, is greater.

Best Conditions for Precipitation

In order to ascertain the effect of variations in the details of procedure a solution containing 20 grams of pure $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 50 cc. of concentrated nitric acid per liter was prepared and standardized by two methods. In the first, 50-cc. portions were evaporated in a platinum dish and the residue was heated cautiously, and finally brought to a temperature sufficient to fuse the resulting bismuth oxide. The weights obtained were 0.2549,

0.2544, and 0.2553 gram. The average value (0.2549) corresponds to 0.3326 gram of BiPO_4 . The bismuth present in 50-cc. portions of the solution was also determined by separating as basic carbonate with a slight excess of ammonium bicarbonate, digesting for a half hour, filtering on a Gooch crucible, and igniting. The results obtained were 0.2548, 0.2541, and 0.2546 gram. The average value (0.2546) corresponds to 0.3321 gram of BiPO_4 . A large number of preliminary quantitative determinations led to the adoption of the following standard procedure:

The acid solution of bismuth was neutralized with ammonium hydroxide until a slight but permanent precipitate was produced; this was then dissolved in 2 cc. of concentrated nitric acid and the volume increased to 100 cc. The solution was heated to boiling, 50 cc. of 0.2 M diammonium hydrogen phosphate, also heated to boiling, were added slowly during the course of about 3 minutes, and the mixture was kept at 80° C. for an hour. The solution was filtered hot on a Gooch crucible, washed three times with 50-cc. portions of hot water, transferred to the crucible with cold water, dried, and ignited to dull redness for a half hour. The results obtained with 50-cc. portions of the standard solution were 0.3319, 0.3322, 0.3317, 0.3319, and 0.3322 gram. The average value is 0.3321 gram.

When the filtrates from these determinations were neutralized with ammonium hydroxide and allowed to stand for 24 hours, no recognizable precipitate separated, nor could bismuth be detected by means of the sulfide test. Two additional determinations, in which the solution was made neutral towards methyl orange before the digestion at 80° C., gave 0.3311 and 0.3319 gram.

Effect of Varying Conditions

The effect of variations from the standard conditions given above is shown in Table I.

TABLE I. WEIGHT OF BISMUTH PHOSPHATE FOUND BY MODIFYING STANDARD PROCEDURE

Variations	BiPO_4 Found Gram
1. 1 instead of 2 cc. of concd. HNO_3 used	0.3317 and 0.3310
2. 4 instead of 2 cc. of concd. HNO_3 used	0.3327 and 0.3325
3. 100 instead of 50 cc. of 0.2 M $(\text{NH}_4)_2\text{HPO}_4$ used	0.3318 and 0.3313
4. 100 instead of 50 cc. of standard bismuth solution used	0.6659 and 0.6630
5. 10 instead of 50 cc. of standard bismuth solution used	0.0653 and 0.0655
6. Precipitate filtered without digesting at 80° C.	0.3311 and 0.3322
7. Precipitate filtered after digesting and allowing to stand 16 hours	0.3310 and 0.3315
8. 3 grams of KNO_3 added	0.3315 and 0.3323
9. 3 grams of NaNO_3 added	0.3321 and 0.3311

These results suggest the following comments: Series 1 and 2 show that H^+ can be increased to unexpectedly large values (at least 0.4 N) without decreasing the yield of precipitate. These findings are at variance with the statement of Schoeller and Waterhouse (1) that the method is decidedly sensitive to variations in H^+ .

Series 3, 4, and 5 indicate that the concentration of soluble phosphate used can be varied within rather large limits without detrimental results. The authors assume this to be due to the relatively slight solubility of the precipitate even in the presence of nitric acid. The much larger concentrations of soluble phosphate recommended by Schoeller and Waterhouse (1) seem unnecessary and result in a greater amount of adsorption of the precipitant used. They assume sufficient phosphate must be added to reduce H^+ to a small value but the authors do not find this necessary.

Series 6 and 7 indicate that the conversion of the basic nitrate into phosphate is usually nearly completed within a few minutes, if the solution is hot and contains sufficient H^+ , and that long standing does not appreciably affect the result. A number of qualitative experiments, in which the rate of

conversion of basic nitrate into phosphate was followed by testing the precipitate for nitrate ion, indicated the desirability of digesting the precipitate for an hour before filtering.

Series 8 and 9 indicate but little error from occlusion of potassium and sodium and the feasibility of precipitating with phosphate of potassium or sodium rather than ammonium.

Separation of Bismuth from Other Ions

The slight solubility of bismuth phosphate in dilute nitric acid suggests the possibility of separating it from a number of metals with which it is frequently associated. Table II gives experiments with 50-cc. portions of the standard bismuth solution, in the presence of certain nitrates.

TABLE II. WEIGHT OF BISMUTH PHOSPHATE
(Found by the standard procedure in the presence of other ions)
Added^a BiPO₄ Found

	Gram
Mg(NO ₃) ₂	0.3324 and 0.3317
Zn(NO ₃) ₂	0.3311 and 0.3323
Cd(NO ₃) ₂	0.3353 and 0.3368
Cu(NO ₃) ₂	0.3323 and 0.3324
Ca(NO ₃) ₂	0.3326 and 0.3341
Pb(NO ₃) ₂	0.3770 and 0.3861

^a 1 gram in each case.

Obviously the separation of bismuth from magnesium, zinc, copper, and calcium by this process offers no difficulty.

The separation from cadmium gives a slight error, probably due to occlusion, and separation from lead, at least under the conditions here suggested, is not possible.

Summary of Results

Bismuth can be accurately determined as the phosphate, if separated from solutions which contain neither Cl⁻ nor SO₄⁻⁻ and are approximately 0.2 M as to nitric acid and approximately 0.065 M as to soluble phosphate. The method is accurate in the presence of moderate concentrations of Na⁺, K⁺, Mg⁺⁺, Zn⁺⁺, Cu⁺⁺, and Ca⁺⁺, gives slightly high results in the presence of Cd⁺⁺, but is not accurate in the presence of Pb⁺⁺.

The chief source of error is the co-precipitation of basic salts; this can be avoided, in the presence of sufficient H⁺, by precipitating from a hot solution with a hot dilute phosphate solution and digesting for an hour at 80° C.

A second possible source of error is the occlusion of small amounts of ammonium phosphate; this can be eliminated by avoiding large concentrations of soluble phosphate, and by igniting the precipitate to 800° C. before weighing.

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RECEIVED June 16, 1936.

Microdetermination of Carbon and Hydrogen

In Compounds Containing Arsenic, Antimony, Tin, Bismuth, and Phosphorus

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DIFFICULTIES have been reported in the literature on the determination of carbon and hydrogen in compounds containing arsenic (10), antimony (9), tin (6), bismuth (7), and phosphorus (1, 2, 3, 5, 8). In some cases these difficulties can be successfully overcome by the addition of suitable materials—e. g., lead chromate, red lead, or copper oxide—to the combustion tube filling and to the sample in the boat. In certain cases these, and other subterfuges, fail and some investigators have determined the carbon only by a wet-combustion method. In many cases no attempt is made to determine either carbon or hydrogen, only the percentage of the metallic element present being determined.

In connection with a study of the exhaustive chlorination of coal conducted in this laboratory, samples which contained appreciable quantities of antimony or phosphorus were submitted for analysis. Since a knowledge of the distribution of the elements of the coal among the reaction products was required in this work, it was important that the carbon-hydrogen content of the samples be known with some degree of accuracy. When the antimony-containing samples were analyzed for carbon and hydrogen by the ordinary micro-procedure using a Pregl Universal tube filling, considerable amounts of a white crystalline substance (antimony oxide) condensed in the constricted end of the combustion tube and in the capillary and forechamber of the Dehydrite-filled absorption tube, which, of course, produced an error in the hydrogen determination. Further, a carbon-hydrogen determination on a pure, known compound made directly following such an analysis yielded erroneous results. In the case of the phosphorus-containing sample there was no visible difficulty, but again a directly succeeding analysis on a pure, known

compound yielded false results, so that no confidence could be placed in the analysis of the phosphorus compound.

Of the methods mentioned in the literature, the modified Dennstedt method recommended by Falkov and Raiziss (4), for the microdetermination of carbon and hydrogen in organic arsenicals and mercurials, seemed most likely to succeed when applied to compounds containing antimony and phosphorus. It was found that a modification of their method could be successfully adapted to the microanalysis of such compounds. The micromethod was first tested on a pure, known organic arsenic compound and the results of Falkov and Raiziss were confirmed. The method was then extended to pure, known compounds containing, respectively, antimony, tin, phosphorus, and bismuth, and was finally applied to the above-mentioned coal samples.

Experimental

The analytical samples, unless otherwise designated, were pure compounds obtained from Eastman. The phosphorus and bismuth compounds were recrystallized from methyl alcohol, the arsenic and antimony compounds from ethyl alcohol, and the tin compound from ether.

Instead of using a Dennstedt catalytic combustion on platinum as recommended by Falkov and Raiziss, a portion of the copper oxide-lead chromate filling of an ordinary Pregl Universal filled combustion tube was removed and replaced by a 3-cm. cylinder made of 200-mesh platinum wire gauze filled with granulated red lead and a 1-cm. plug made of platinum wire gauze. The red lead was prepared by igniting Merck's lead peroxide (*pro analysi, granuliert nach Pregl*), in a stream of oxygen in a microcombustion tube in an electric combustion furnace at the normal combustion temperature. To prevent any red lead dust from sifting

TABLE I. RESULTS OF ANALYSIS

Sample No.	Substance	Weight of Sample Mg.	Found				Difference from Theory		Metal %
			H ₂ O Mg.	CO ₂ Mg.	H %	C %	H %	C %	
1	C ₁₈ H ₁₈ As Triphenylarsine	3.524	1.517	9.109	4.82	70.50	-0.12	-0.08	24.48 As
		3.616	1.619	9.382	5.01	70.76	+0.07	+0.18	24.48 As
		4.619	2.011	11.940	4.87	70.50	-0.07	-0.08	24.48 As
				Mean =	4.90	70.59	-0.04	+0.01	
2	C ₁₈ H ₁₈ Sb Triphenylstibine	3.107	1.164	6.965	4.19	61.14	-0.10	-0.07	34.51 Sb
		3.054	1.185	6.842	4.34	61.11	+0.05	-0.10	34.51 Sb
		4.708	1.838	10.540	4.37	61.06	+0.08	-0.15	34.51 Sb
		4.152	1.614	9.301	4.35	61.10	+0.06	-0.11	34.51 Sb
		5.443	2.137	12.210	4.39	61.18	+0.10	-0.03	34.51 Sb
		4.142	1.588	9.284	4.29	61.13	0.00	-0.08	34.51 Sb
				Mean =	4.32	61.12	+0.03	-0.09	
3	C ₁₈ H ₁₆ Cl ₂ Sb Triphenylstibinic chloride ^a	4.530	1.517	8.437	3.75	50.80	+0.18	-0.17	28.73 Sb
		2.932	0.933	5.472	3.56	50.90	-0.01	-0.07	28.73 Sb
		3.666	1.206	6.855	3.68	51.00	+0.11	+0.03	28.73 Sb
		5.533	1.726	10.360	3.49	51.07	-0.08	+0.10	28.73 Sb
		3.580	1.181	6.675	3.69	50.85	+0.12	-0.12	28.73 Sb
		2.920	0.955	5.471	3.66	51.10	+0.09	+0.13	28.73 Sb
		3.677	1.188	6.875	3.62	50.99	+0.05	+0.02	28.73 Sb
		4.573	1.523	8.493	3.73	50.65	+0.16	-0.32	28.73 Sb
		3.920	1.282	7.298	3.66	50.77	+0.09	-0.20	28.73 Sb
				Mean =	3.65	50.90	+0.08	-0.07	
					1.54	22.07	0.00	+0.14	37.09 Sb
4	C ₈ H ₅ O ₅ NCISb 2-Chloro-5-nitrophenylstibonic acid ^b	3.934	0.540	3.183	1.78	22.22	+0.24	+0.29	37.09 Sb
		4.119	0.657	3.356	1.67	21.92	+0.02	-0.01	37.09 Sb
		3.987	0.557	3.204	1.56	21.83	+0.13	-0.10	37.09 Sb
		4.678	0.700	3.745	1.87	21.93	+0.33	0.00	37.09 Sb
		5.081	0.847	4.085	1.59	22.02	+0.05	+0.09	37.09 Sb
		3.108	0.441	2.509	1.65	21.91	+0.11	-0.02	37.09 Sb
		3.517	0.517	2.826	1.67	21.89	+0.13	-0.04	37.09 Sb
		3.570	0.532	2.865	1.67	21.97	+0.13	+0.04	
				Mean =	1.67	21.97	+0.13	+0.04	
					5.87	82.52	+0.10	+0.12	11.83 P
5	C ₁₈ H ₁₈ P Triphenylphosphine	4.280	2.245	12.950	5.80	82.37	+0.03	-0.03	11.83 P
		3.511	1.820	10.604	5.81	82.51	+0.04	+0.11	11.83 P
		3.560	1.848	10.770	5.83	82.47	+0.06	+0.07	
6	C ₂₆ H ₂₇ O ₄ P Tri- <i>o</i> -phenylphenyl phosphate	3.531	1.579	10.097	5.00	77.99	+0.09	+0.04	5.60 P
		3.473	1.546	9.920	4.98	77.90	+0.07	-0.05	5.60 P
				Mean =	4.99	77.95	+0.08	0.00	
7	C ₁₈ H ₁₅ O ₃ SP Triphenylthiophosphate	3.291	1.324	7.626	4.50	63.20	+0.08	+0.08	9.07 P
		4.275	1.734	9.915	4.54	63.25	+0.12	+0.13	9.07 P
		3.553	1.374	8.240	4.33	63.25	-0.09	+0.13	9.07 P
				Mean =	4.46	63.23	+0.04	+0.11	
8	C ₁₈ H ₁₅ Bi Triphenylbismuthine	3.804	1.257	6.866	3.70	49.23	+0.26	+0.15	47.49 Bi
		3.674	1.176	6.627	3.58	49.19	+0.14	+0.11	47.49 Bi
				Mean =	3.64	49.21	+0.20	+0.13	
9	C ₁₈ H ₁₅ Cl ₂ Bi Triphenylbismuthine dichloride	4.372	1.196	6.730	3.06	41.98	+0.10	-0.29	40.90 Bi
		5.756	1.567	8.876	3.05	42.06	+0.09	-0.21	40.90 Bi
		5.191	1.430	8.049	3.08	42.29	+0.12	+0.02	40.90 Bi
				Mean =	3.06	42.11	+0.10	-0.16	
10	C ₁₈ H ₁₅ ClSn Triphenyltin chloride	3.527	1.261	7.275	4.00	56.25	+0.08	+0.19	30.81 Sn
		3.521	1.291	7.251	4.10	56.16	+0.18	+0.10	30.81 Sn
				Mean =	4.05	56.21	+0.13	+0.15	

^a Prepared in this laboratory by J. F. Weiler.
^b Kindly supplied through the courtesy of C. S. Hamilton of the University of Nebraska.

through the platinum gauze, a thin layer of asbestos lined the entire inner surface of the cylinder, including the ends. This snug-fitting cylinder ensured more intimate contact of the combustion gases with the red lead than if the latter was merely placed in a boat, as recommended by Falkov and Raiziss. The details of the filling are illustrated in Figure 1.

The samples were burned by the usual procedure, the water formed being absorbed on Dehydrite and the carbon dioxide on Ascarite. In the case of the phosphorus compounds a carbonaceous deposit formed on the inner surface of the combustion tube just adjacent to where it entered the electric combustion furnace; in order to remove this carbon quanti-

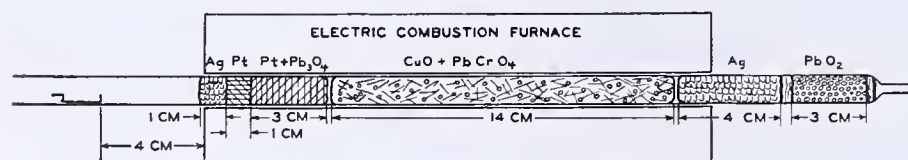


FIGURE 1. COMBUSTION TUBE FILLING

tatively the combustion tube had to be strongly heated on all sides with a bare Bunsen flame. The antimony, bismuth, and tin compounds left a white deposit (antimony, bismuth, and tin oxides) on the inner surface of the combustion tube which could not be removed even on strong heating. In the case of the antimony compounds especially, it was observed that some

of the compound distilled into the portion of the combustion tube surrounded by the heated furnace while a portion remained outside; the latter, on being subjected to the heat from the Bunsen burner, decomposed leaving a residue on the inner glass surface. That material which distilled into the combustion tube suffered thermal decomposition and the antimony oxide was absorbed by the platinum-red lead filling, apparently forming lead antimonate. In no case, when using this filling, was any deposit of crystalline material observed in the constricted end of the combustion tube or in the capillary or forechamber of the water-absorption tube. After a

number of such antimony-containing samples had been burned it was noticed that the platinum acquired a definite bluish iridescence and the surface of the red lead granules was coated with a yellow incrustation. After analysis of some of the other compounds, the red lead was also partially covered with a grayish metallic looking coating.

Results

The results of the analysis of these compounds are summarized in Table I.

The carbon-hydrogen values on the arsenic, antimony, and phosphorus compounds are accurate to about 0.1 per cent and the bismuth and tin compounds to about 0.2 per cent. Calculation of the observed and theoretical carbon-hydrogen

ratios for all these substances revealed that, if this observed ratio (for the C_{18} compounds) was not in error by more than about 3 per cent, the correct number of hydrogen atoms were obtained by calculation, assuming the theoretical number of carbon atoms to be present. With errors greater than 3 per cent, however, the number of hydrogen atoms calculated would be in error by one unit; such was the case for samples 8 and 9. In the case of the C_6 compound the error in the carbon-hydrogen ratio can be three times larger without making the error in the calculation of the number of hydrogen atoms any greater.

Summary

1. The determination of carbon and hydrogen in compounds containing arsenic, antimony, tin, phosphorus, and bismuth using the ordinary Liebig or Pregl procedure is extremely difficult or even impossible.

2. By a modification of the Falkov-Raiziss macromethod, the microdetermination of carbon and hydrogen in the above compounds can be successfully performed. The important

feature of the method consists in the introduction of a layer of platinum gauze and of red lead as an integral part of the combustion tube filling to remove metallic oxides which otherwise vitiate the results.

3. The results on the arsenic, antimony, and phosphorus compounds are accurate to about 0.1 per cent and on the bismuth and tin compounds to about 0.2 per cent.

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Determination of Neutral Equivalents of Higher Fatty Acids

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IN CONNECTION with studies of certain binary systems of the higher fatty acids and with studies of synthetic fats (6), it was felt that improvements might be made in the ordinary method for determining the neutral equivalent of a higher fatty acid. The customary procedure is to dissolve a given weight of the fatty acid in enough alcohol, neutral to phenolphthalein, to make the alcohol content at least 50 per cent at the end of the titration. The alcoholic solution is then titrated with aqueous alkali, phenolphthalein being the indicator. The authors have found through considerable experience that, in spite of the apparent simplicity of the procedure, to get reproducible and accurate results requires considerable skill.

Bishop, Kittredge, and Hildebrand (1) have called attention to the fact that the use of alcohol as a solvent in acid-base titrations may be advantageous for two reasons: Its solvent power for certain substances, such as the fatty acids, which are not soluble in water; and the somewhat greater sharpness of the end points obtainable (3). With this view in mind, Hildebrand and co-workers (1) have prepared an indicator scale for alcoholic solutions similar to those in common use for aqueous solutions. They have shown that palmitic acid, for example, is neutralized by sodium ethylate at about 0.8 volt, so that thymolphthalein should change color close to the true end point. Kolthoff and Furman (4) have also pointed out that alcohol lowers the dissociation constants of both weak acids and indicators. In addition, the ion product of water is much smaller with increasing alcohol content.

The method for determining the neutral equivalent of a fatty acid of high molecular weight, described in this paper, involves titrating the acid in absolute alcohol solution, with sodium ethylate as the base, using thymolphthalein as the indicator, as suggested by Hildebrand. The advantage of a two-color indicator is obvious, and a combination of methyl orange and thymolphthalein has been found to be a distinct advantage. The color change is from yellow to green and is very readily detected. To make the end point even more

readily determined, the titration is performed in a Nessler tube. Finally, the primary acid standard, which has been found to be very satisfactory, is a highly purified grade of stearic acid.

Reagents and Apparatus

The purification of the alcohol and the preparation of the sodium ethylate (0.05 N) were carried out according to Bishop, Kittredge, and Hildebrand (1).

The sodium ethylate was stored in a flask under an atmosphere of purified hydrogen furnished by a Kipp generator. The sodium ethylate solution was delivered to a 10-cc. buret, divided into 0.05 cc., attached to the flask in such a way that the solution was forced over by the hydrogen pressure. By maintaining a constant positive pressure of hydrogen in the main reservoir, the ethylate solution could be kept colorless for several weeks at a time. The titration was performed in a 50-cc. Nessler tube (about 16 cm. internal diameter) set in a wooden rack finished in dull black and fitted with an opal glass reflector set at an angle at the bottom. Stirring could be carried out by bubbling tank nitrogen through the solution, or, because of the small area of solution exposed to the air, with a ring stirrer made from glass rodding.

The sodium ethylate was standardized against pure stearic acid. To obtain a stearic acid sufficiently pure for this purpose, Eastman Kodak Company stearic acid of melting point 69° to 70° C. was crystallized from acetone until a constant capillary melting point of 69.6° to 69.8° C. (5) was obtained. It was then dried *in vacuo* over sulfuric acid in an Abderhalden drier (2) and at the temperature of boiling water. The remaining fatty acids used in the experimental work were Eastman products, purified by repeated crystallization from acetone and dried in the same way as the stearic acid. The palmitic acid had a melting point of 62.4° to 62.7° C., myristic acid 54.4° to 54.8° C., and lauric acid 44.1° to 44.3° C. The thymolphthalein indicator solution was made by dissolving 0.5 gram of the indicator in 100 cc. of alcohol. The methyl orange solution was made by dissolving 0.2 gram of the dye in 1 liter of water.

Procedure

Weigh into a Nessler tube not over 0.15 gram (a quantity which will require from 9 to 10 cc. of 0.05 N sodium ethylate solution) of the fatty acid. Add 10 cc. of the purified alcohol, taking care to wash down any particles of fatty acid clinging to the walls of the tube. Add 5 drops of thymolphthalein indicator and 3

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TABLE I. NEUTRAL EQUIVALENTS OF FATTY ACIDS

	Calcd.	Found	Semi-micromethod Calcd.	Found
Palmitic acid	256.3	256.5 256.8	256.3	255 256
Lauric acid	200.2	200.2 200.0	200.2	200 201 199
Myristic acid	228.2	227.7 228.0	228.2	229 227 227

drops of methyl orange. Heat the tube in water at 65° C. to ensure complete solution of the fatty acid, and titrate the acid with the standard ethylate solution. Use a ring stirrer and near the end point stir vigorously after each drop. Take the first appearance of green as the end point; it is quite distinct. Use a control tube containing 20 cc. of alcohol and 3 drops of methyl orange. Carry out a blank determination on 10 cc. of alcohol and subtract this value from the actual run. Standardize the sodium ethylate against pure stearic acid in a similar manner.

A few typical analyses, listed in Table I, indicate the real value of the method. Results which were carried out on a semi-microscale, using not more than 50 mg. of fatty acid and 0.017 N sodium ethylate, are also included.

Acknowledgment

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Determination of Ferrocyanide Ion by Means of Luteocobaltamine Chloride

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WILLIAMS (19) listed several procedures for the estimation of ferrocyanides. Of these, his own method (20) seems to be the most accurate of the processes proposed up to that time. Hurter (10), Knublauch (11), and Zaloziecki (21), recommending titration with zinc and copper salts, were adversely criticized by several analysts, including Colman (3) and Lunge (13), the latter claiming that only 79 to 85 per cent of the ferrocyanide content determinable by precipitation as Prussian blue could be obtained by this process, while Leeds (12) claimed that precipitated Prussian blue always gives results which are too low when ignited to the oxides. Skirrow (16) unfavorably criticized Feld (7) for his use of magnesium and mercury salts, but Colman (4) defended the use of Feld's procedure and challenged Skirrow's analytical results.

The method proposed here is of approximately the same accuracy as that of Williams (20), which requires slightly less than 2 hours for completion, and which demands the attention of the operator continuously during the course of the analysis. In addition, the end point obtained on titrating the cyanide with silver nitrate (the first appearance of a permanent opalescence) is somewhat unsatisfactory and requires considerable practice on the part of the analyst until he becomes familiar with its appearance under varying conditions—viz., light, background, etc.

A number of oxidimetric methods for the determination of the ferrocyanide present in both pure salts and gas-furnace residues have been proposed. These methods involve oxidation of the ferrocyanide by means of potassium permanganate (18), potassium dichromate, ammonium persulfate, potassium bromate, and ceric sulfate. Some of these are strictly volumetric, while others are potentiometric in nature. The latest, involving potentiometric titration with ceric sulfate, was found accurate and ideal for routine analysis (8), but the other oxidimetric methods seem to have as many critics as they have proponents and defenders. Hence, they were not considered as controls in this work.

Luteocobaltamine chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, is prepared

according to Biltz, Hall, and Blanchard (1), recrystallized, and dried to constant weight, the purity of the compound being then established by gravimetric determination of the chloride ion.

The luteo salt reacts with ferrocyanide ion in neutral aqueous solutions to form luteocobaltamine ferrocyanide, $[\text{Co}(\text{NH}_3)_6]_4[\text{Fe}(\text{CN})_6]_3$, first reported by Gibbs and Genth (9), and later by Braun (2). Ephraim and Mosimann (5) also prepared this compound, and Steinmetz (17) studied its crystallographic properties. These authors state that the compound is difficult to analyze because of the presence of adherent moisture, and for this reason recommend either ignition to oxides of the metals present followed by reduction to the free metals, or decomposition of the compound with concentrated sulfuric acid followed by gravimetric determination of the sulfates. All agree that the substance is almost insoluble in water. Steinmetz specifically states that it is markedly more soluble in hot water, from which it does not separate unchanged, and that it is rather easily soluble in warm 20 per cent ammonium chloride solution, from which crystals of measurable size separate. Measurable crystals also form from solutions in dilute hydrochloric acid, provided the concentration of the acid is not increased by evaporation. The authors have found, as was to be expected, that the compound is also insoluble in organic solvents.

No data can be found in the literature as regards the actual solubility of the luteocobaltamine ferrocyanide, and the authors' attempts to determine the solubility of this salt have not been successful, probably because of decomposition of the suspended salt in pure water at 20° C. The results obtained varied between 52 and 66 mg. per liter. The suspension tends to become olive-green after agitation with water for 2 hours, the color deepening as time goes on, until at the end of a week a greenish sediment appears mixed with some of the original material. This was not analyzed because of difficulty of separating the two substances.

It was found impossible to use the hexamminocobaltic

ferrocyanide as a gravimetric determinant for ferrocyanide ion, because of its instability as shown by the following experiments: On exposure to acidic drying agents—e. g., phosphorus pentoxide or concentrated sulfuric acid—decomposition occurred. At the temperature of boiling ether in an Abderhalden drier, approximately 72 hours were required for this decomposition. The result was a tan-colored product from which the original compound could be regenerated by exposure to ammonia vapors. At the temperature of boiling water, a dark-brown, almost black, substance was obtained in 48 hours, from which the original salt could not be regenerated on exposure to ammonia fumes. Further work is in progress on these decomposition products.

Under the conditions prevailing during the determination of ferrocyanide ion by this procedure, of the commoner anions only chromate, dichromate, and metavanadate ions interfere. Parks (14) and Parks and Prebluda (15), in fact, suggest the use of this reagent for gravimetric quantitative determination of vanadium. Ferricyanide ion, contrary to the statements found in the literature, did not precipitate under these conditions, and, as was pointed out to the authors (in a private communication from V. K. LaMer, who stated that he had suggested use of such complex salts as qualitative and quantitative reagents some years ago), this may have been due to relatively high concentrations of the anions or to the order of addition of the reagent and test solutions, although this latter consideration seemed of no influence in the case of the ferrocyanide.

Quantitative Procedure

Salt used: crystalline potassium ferrocyanide.

Reagent: 0.15 *M* aqueous solution of hexamminocobaltic chloride.

METHOD. Weigh out 0.1 to 0.2 gram of the ferrocyanide in a 125-ml. beaker, and dissolve the sample in 15 to 20 ml. of water. To this solution add sufficient reagent to assure complete precipitation. Allow the precipitate to settle and filter through a Gooch crucible which has been ignited to constant weight. Wash thoroughly with ice water (distilled water kept in the refrigerator will suffice for this purpose) to remove excess reagent. The washing may be considered complete when the filtrate is no longer colored. Care must be taken to use the minimum amount of wash water, as an excess tends to lower the results.

Dry the crucible in an oven at 100° to 110° C. for 0.5 hour. Ignite slowly over a Bunsen burner until the entire mass in the crucible has ceased to glow. Then ignite strongly for about 30 minutes over a Meker-type burner. On ignition over the Bunsen burner, ammonia and hydrocyanic acid gases can be readily detected. Cool and weigh.

The computations in Table I are based on the assumption that the precipitate is $[\text{Co}(\text{NH}_3)_6]_4[\text{Fe}(\text{CN})_6]_3$. Thus, from 18 $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ the ignited precipitate contains $3\text{Co}_2\text{O}_3 + 9\text{Fe}_2\text{O}_3$.

In this determination, the amount of ferrocyanide ion remaining in the filtrate and appearing in wash water has been found insufficient to react directly with ferric chloride and hydrochloric acid to give Prussian blue. On prolonged boiling with concentrated sulfuric acid, ferric hydroxide could not be precipitated in the acid liquid on treating with excess ammonium hydroxide.

From the mixed ignited oxides it was calculated that

$\text{Co}:\text{Fe} = 1:0.7028$. On determining the iron by Rothe's ether method followed by Zimmermann-Reinhardt determination, it was found that $\text{Co}:\text{Fe} = 1:0.6838$. Fales (6) states that this method is slightly low for iron. From $\text{Co}_{24}\text{Fe}_{18}\text{O}_{53}$, iron should be theoretically 41.12 per cent and on reducing the ignited metals with hydrogen an average of 40.61 per cent of iron was found.

TABLE I. DETERMINATION OF FERROCYNIDE ION

No.	Sample Gram	Oxides Gram	Fe(CN) ₆		Recovery %	Difference %
			Calcd. Gram	Found Gram		
1	0.1043	0.0461	0.05232	0.05227	99.90	-0.10
2	0.1007	0.0442	0.05052	0.05012	99.21	-0.79
3	0.1180	0.0520	0.05920	0.05896	99.60	-0.40
4	0.1222	0.0539	0.06130	0.06112	99.70	-0.30
5	0.1097	0.0485	0.05500	0.05500	100.00	0.00
6	0.1783	0.0783	0.08945	0.08878	99.25	-0.75
7	0.1547	0.0681	0.07760	0.07722	99.51	-0.49
8	0.1133	0.0500	0.05680	0.05670	99.82	-0.18
9	0.1565	0.0692	0.07850	0.07847	99.96	-0.04
10	0.1846	0.0814	0.09261	0.09230	99.66	-0.34

Av. 99.66

Conclusions

Luteocobaltamine chloride may be used as a quantitative precipitant for the ferrocyanide ion, in the absence of chromate, dichromate, and metavanadate ions.

Results compare favorably with standard methods.

This method does not require much skill on the part of the operator, nor is his attention required except during the actual precipitation, filtration, and first stage of the ignition, a total of approximately 25 minutes.

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Approach towards the Limit in the Process of Extraction

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IN AN EARLIER paper (2) it was shown that for the process of extraction the formula

$$X_n = X_0 \left[\frac{KW}{KW + L/n} \right]^n \quad (1)$$

where W = cc. of solution
 X_0 = grams of solute
 L = total cc. of extracting solvent
 K = distribution ratio of the solute for the two solvents
 X_n = grams of solute remaining unextracted after the n th extraction

may be employed to calculate the amount of solute which may be expected after a given number of operations (the number of operations being varied by dividing the L cc. of extractant into $L/2$, $L/3$. . . or L/n cc. portions where 2, 3 . . . or n extractions are to be made); and the limit of X_n/X_0 as n approaches infinity was found to have the value $e^{-L/KW}$.

The object of the present study has been to learn just how closely the experimental results follow the theoretical path for the approach of X_n/X_0 towards its limit, $e^{-L/KW}$, as n takes on increasing values. In three of the four cases studied little or no disturbance from such influence as dissociation or association occurs. In one case, where acetic acid was used as the distributed substance, the results, uncorrected for such disturbance, are in good agreement with the theoretical.

The procedure in the four cases investigated was first to select suitable values for L , W , and X_0 . These quantities were chosen so that the concentrations of the solute in the two solvents would approximate initially the conditions used by previous workers in their determinations of K , the distribution constant. Of course the concentration of the solute diminishes rapidly with each extraction; this is only

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one reason why the experimental path of X_n/X_0 plotted against n might not coincide with the calculated curve. (Another reason would be, as Hill, 6, points out in connection with constancy of K , the slight solubility of one liquid phase in the other. In one case in the present study this factor caused a rather wide divergence between the observed and the calculated curve.)

After dissolving the solute in the W cc. of solvent one portion of L cc. of extracting liquid was added and the mixture shaken in a separatory funnel placed in a water bath kept at a temperature of $25.0 \pm 0.02^\circ \text{C}$. In general the mixture remained in the thermostat one day and was then removed, and the layers were separated and analyzed. The first experiment, using L cc. of extractant, was in every case to check the value of K as found by previous investigators. If the result confirmed the value of K found in the literature, it was assumed that sufficient time had elapsed for attainment of equilibrium, but as an additional check upon this point the solute was frequently dissolved initially in the L cc. of the one solvent instead of in the W cc. of the other before mixing the two.

After the first run, others followed which differed from the first only in that L/n cc. of extracting liquid were used in n successive portions, the second portion replacing the first after the first had reached equilibrium with the W cc. of original solution, and so on. Analysis was finally made to determine X_n , the amount of distributed substance remaining unextracted. Furthermore, the total amount of solute—i. e., that in the W cc. and in, for example, the two $L/2$ -cc. portions of extractant—was determined as a check against the weight, X_0 , originally taken.

In the figures the theoretical curve for X_n/X_0 against n has been plotted in each case by calculating sufficient points for X_n/X_0 from Formula 1. The limiting value for X_n/X_0 as $n \rightarrow +\infty$ (shown by broken curves in the figures) has been computed from the constant $e^{-L/KW}$.

The points designated in the figures by circles represent the experimental values as obtained by analysis for X_1/X_0 , X_2/X_0 , X_3/X_0 , etc. The extent by which these fail to fall

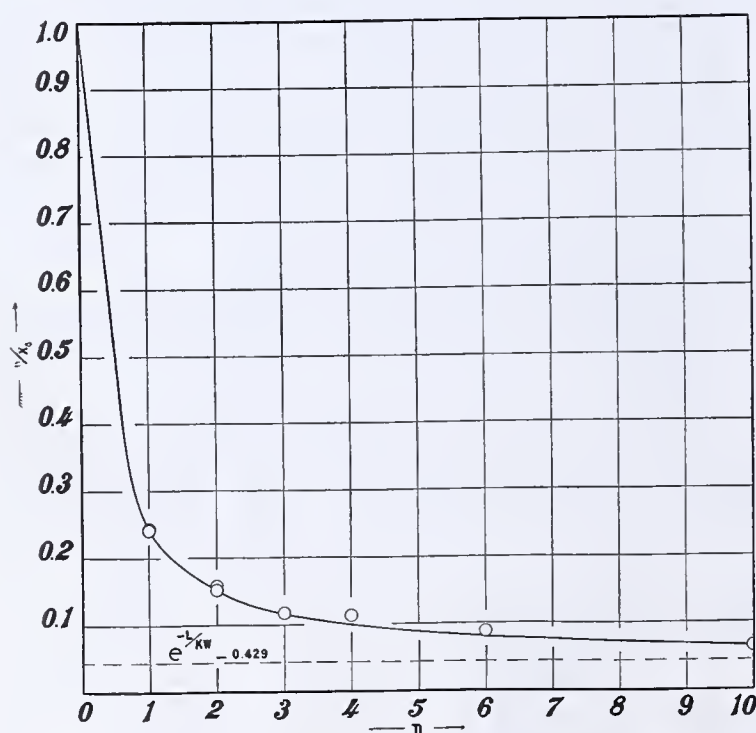


FIGURE 1. EXTRACTION OF BORIC ACID FROM ISOAMYL ALCOHOL WITH WATER

W , 100 cc.
 L , 100 cc.
 X_0 , 1.5 grams

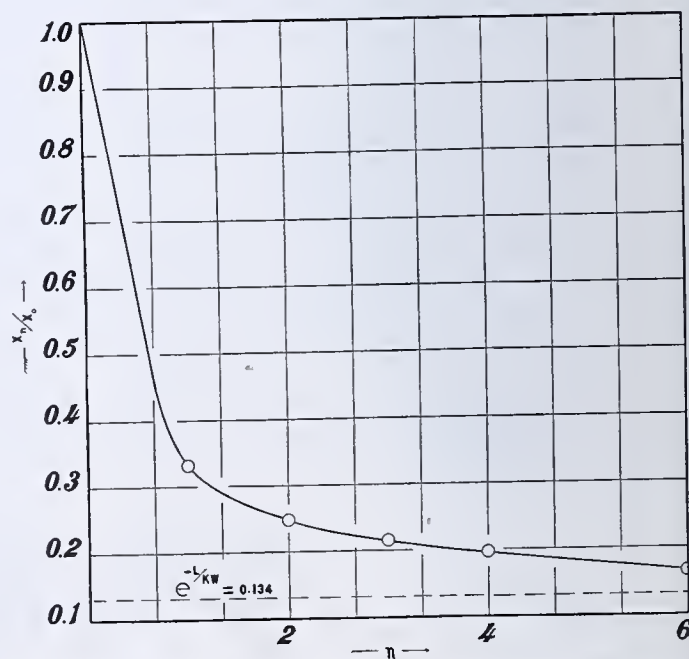


FIGURE 2. EXTRACTION OF IODINE FROM WATER WITH CARBON TETRACHLORIDE

W , 1000 cc.
 L , 24 cc.
 X_0 , 0.1 gram

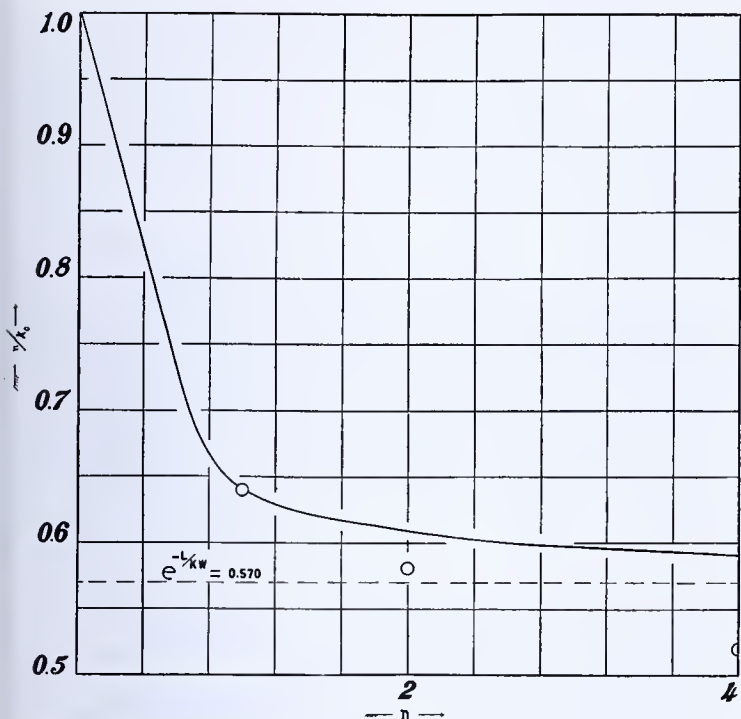


FIGURE 3. EXTRACTION OF IODINE FROM ETHER WITH ETHYLENE GLYCOL
 W , 200 cc.
 L , 200 cc.
 X_0 , 0.4 gram

upon the theoretical curve therefore represents the departure of the experimental facts from the theoretical.

X_0 was always weighed to 0.1 mg. and volumes in titrations were read to 0.01 cc. It is therefore believed that the precision of the experiments was limited by the values of K which were employed in the calculations with three significant figures.

The chemicals used were c. p. products from the Eastman Kodak Company and Merck and Co. They purposely were not further purified, since a higher purity would be impracticable in large-scale operations.

In every case the standard solutions used in making analyses were standardized against the substance used as the distributed solute.

Extraction of Boric Acid from Isoamyl Alcohol with Water

Abegg, Fox, and Hertz (1) found the value of the distribution constant for this system to range, for varying concentrations, from 3.47 to 3.27 (concentration in water/concentration in alcohol). The results of the present work gave a value of 3.15. The reciprocal, $1/3.15$, was employed in the authors' calculations since in Formula 1 K must be defined as concentration in original solution/concentration in extracting phase.

Boric acid was determined by titrating the water and the alcohol phases with standard sodium hydroxide solution. Glycerol was employed instead of mannitol, and phenolphthalein was used as the indicator.

As shown in Figure 1, six points were secured in this case with a maximum value of 10 for n . The experimental points are in very good agreement with the theoretical curve and with $n = 10$, over 93 per cent of the boric acid has been extracted from the alcohol.

Extraction of Iodine from Water with Carbon Tetrachloride

Jakowkin (4) found the distribution constant for this system to range for a fivefold variation in concentration from 37.9 to 85.8. The determination of K in this work yielded a

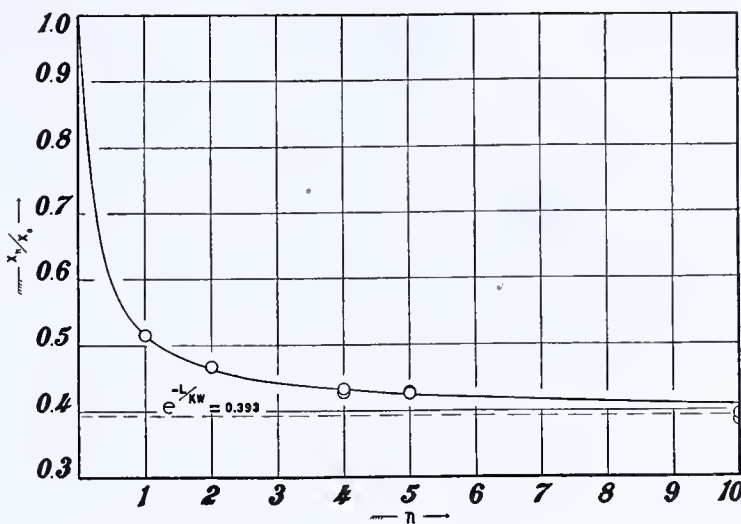


FIGURE 4. EXTRACTION OF ACETIC ACID FROM ISOAMYL ALCOHOL WITH WATER
 W , 100 cc.
 L , 100 cc.
 X_0 , 5.0 grams

value of 83.9. The reciprocal, 0.0119, was used for calculations.

Great care must be exercised to effect a complete separation of the tetrachloride with its dissolved iodine from the aqueous solution. Many extremely small droplets of tetrachloride are very slow in settling and the small but significant quantities of the solvent may be repeatedly obtained by whirling the mixture in the separatory funnel.

Carbon tetrachloride is slightly soluble in water, but the rate of solution is so much slower than attainment of the distribution equilibrium that its solubility is negligible.

The solutions were analyzed, after separation of the two layers, by titrating with standard sodium thiosulfate solution. Potassium iodide was first added and starch was used as the indicator.

This case is particularly interesting in that here W was taken some forty times larger than L . Even so the results show a good concordance between the experimental and the theoretical points.

Figure 2 gives the curve for this system. Five experimental points were obtained with a maximum value of 6 for n . The coincidence of the observed points and the calculated curve for this case is the closest of all studied. Even with the ratio of $W:L$ being 41:1, the extraction of the iodine when $n = 6$ is found to be over 82 per cent.

Extraction of Iodine from Ether with Ethylene Glycol

Landau (5) found the value of the distribution constant for this system to be 1.78. The present study confirmed this figure. Landau, after separating the two phases, added ethyl alcohol to the ether phase until a homogeneous solution was formed. He then added potassium iodide and titrated nearly to the end point with standard sodium thiosulfate solution, after which starch was added and the titration completed. In this work more consistent results were obtained by omitting the use of ethyl alcohol.

When ethylene glycol and ether are mixed the ether layer diminishes in volume to a considerable extent; thus with each glycol extraction W becomes less. This means that the iodine removed by the glycol will become progressively greater than if no such diminution occurred. As a result, as seen in Figure 3, X_n , and thus also X_n/X_0 , are less than theoretically calculated, and the observed points fall below the curve. In fact when $n = 4$ the extraction has proceeded to 48 per cent, whereas theoretically it should be only 41 per cent.

Extraction of Acetic Acid from Isoamyl Alcohol with Water

Hertz and Fischer (3) determined the distribution constant for this system at 20° C., and obtained a value of 0.923. In this study the constant, uncorrected for dissociation, at 25° C. was found to be 0.936. Employed in the calculations for the purpose at hand the value 1/0.936, or 1.07, was used. Analyses of the two layers for acetic acid content were made by titrating with standard sodium hydroxide solution.

Figure 4 shows the five points obtained in this case. All experimental points except for $n = 10$ are very near the theoretical curve. Duplicate runs for $n = 10$ yielded points, both of which fall slightly below the curve. It should be pointed out that this case is different from that shown in Figure 3 where the experimental points fell progressively further below the curve as n took on increasing values. In

the present case, although, because of increased dissociation of acetic acid in the aqueous phase with greater dilution, more efficient extraction would be expected as n is increased, nevertheless the dissociation of acetic acid for concentrations prevailing when $n = 1$ and when $n = 10$ is of the same order of magnitude; only when n takes on high values would dissociation prove an important factor.

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Solubility of Naringin in Water

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THE possibility of utilizing grapefruit residue for the production of naringin and its hydrolytic products, together with the fact that there is a limited commercial production of naringin at the present time, has shown the desirability of determining the solubility of naringin in water at various temperatures.

Naringin ($C_{27}H_{32}O_{14} \cdot 2H_2O$) was discovered by DeVry (2) in the flowers of grapefruit trees growing in Java. Will (6, 7, 8), Zoller (9), and Asahina and Inubuse (1) have conducted studies to determine its properties. Its increased solubility in hot water or juice has been noted by Fellers (3), and Segal and de Kiewiet (5) in technological studies on grapefruit products. The content of naringin in both peel and juice appears to diminish as the fruit matures. It is soluble in alcohol, acetone, and water. When crystallized from these solvents and dried at 110° C. it melts at 171° C. When crystallized from water it has an additional 6 molecules of water and melts at 83° C. The bitter taste of naringin is pronounced: a water solution containing one part in ten thousand has a distinctly bitter taste.

The naringin used in these experiments was made from grapefruit peel, purified by the method outlined by Poore (4) and dried at 110° C.; the melting point was 171° C. (uncor.).

The solubility of naringin was determined by adding an excess of the purified material to 150 cc. of distilled water contained in a flask which was closed with a rubber stopper and immersed in a constant-temperature water bath. The flask was left in the bath 2 hours and was shaken every 15 minutes. At the end of 2 hours the solution in the flask was rapidly filtered, using a

water-jacketed funnel. A measured volume of the clear filtrate was transferred to a weighed evaporating dish and evaporated to dryness over a steam bath, then dried at 110° C., cooled, and weighed. The amount of naringin dissolved per 1000 cc. was calculated from the average of two determinations.

The solubility at 6° C. was determined by placing the flasks in an electric refrigerator, while the solubility at 20° C. was determined in an ice-cooled box. The variation in the temperature at these two points was greater than at the higher temperatures, but, since the increase in solubility of naringin between 6° and 35° is so small, fluctuations in temperatures at 6° and 20° C. would have no significant effect upon the solubility value. Solubilities at other temperatures were carried out in a water bath, the temperature of which was controlled by means of a gas thermoregulator. The water in the bath was kept in constant motion by means of compressed air.

The data given in Table I and Figure 1 show that up to 45° C. the increase in solubility with increase in temperature is not pronounced. From 45° C. to the melting point (83° C.) the solubility increases rapidly with increase in temperature.

TABLE I. SOLUBILITY OF NARINGIN IN WATER

Temperature of Water ° C.	Solubility in Water G./1000 cc.
6	0.17
20	0.50
35	0.79
45	1.96
55	7.16
65	42.21
75	108.24

The decreased solubility of naringin at low temperatures may at times cause the precipitation of this substance in canned grapefruit juice and sections, as has been pointed out by Fellers and by Segal and de Kiewiet (5). This is especially true if the juice or sections have been prepared from immature or frozen fruit. In the case of canned juice the glucoside generally settles to the bottom of the container as a yellow sludge. Sections may show light yellow spots, which macroscopically have the appearance of mold. At times the juice has a milky appearance due to minute crystals of naringin.

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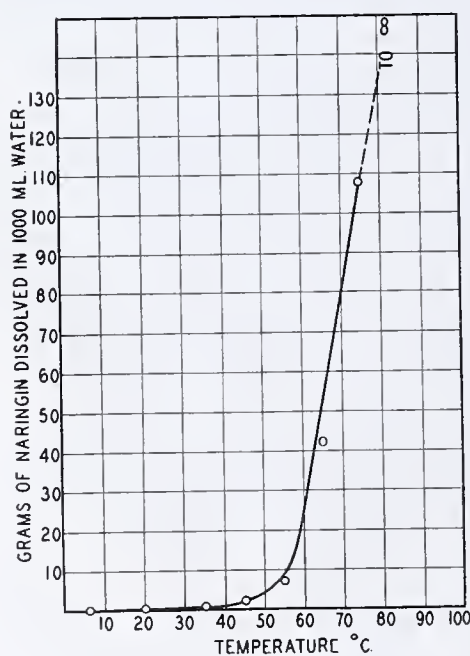


FIGURE 1

Determination of Basic Nitrogen

A Semi-Micromethod Applicable to Plant Tissues

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AS WAS discussed in a previous paper (11), the limitations of plant culture work frequently necessitate the use of semi-micromethods in the study of nitrogen metabolism. Since methods for basic nitrogen have not been always suitable for semi-micromodification, a study of those which might be applied to plant materials where the presence of carbohydrate and other constituents influences the precision was undertaken. With the use of a modified technic reported here, the quantitative estimation of this fraction was possible with a precision and accuracy comparable to that obtained in the protein studies.

The method for the preparation of the plant sap, hydrolysis, and amide estimation are discussed by Orcutt and Wilson (9). Briefly, the soluble nitrogen constituents are removed from the tissue by pressure, the coagulable materials precipitated by heat, the remaining peptides hydrolyzed without formation of humin by an enzyme preparation and amides hydrolyzed by sodium bisulfite, and the ammonia thus liberated is estimated by aëration. The sap so obtained is neutralized, water is added to a definite volume, and aliquots are taken for precipitation. Using such peptide-, amide-, and ammonia-free saps, the factors influencing the semi-micro quantitative precipitation and determination of basic nitrogen with phosphotungstic acid were studied.

Precipitation Method for Basic Nitrogen

The material remaining after the removal of amide (9) is titrated with glacial acetic acid until it is just acid to phenolphthalein, and made up to 25 cc. A 20-cc. aliquot of this is placed in a 50-cc. beaker and 1.1 cc. of 20 *N* sulfuric acid are added, together with 2 cc. of the phosphotungstic acid reagent. This reagent is composed of 20 grams of the 1 to 24 phosphotungstic acid ($P_2O_5 : 24WO_3 \cdot xH_2O$) and 3 cc. of concentrated sulfuric acid made up to 100 cc. with distilled water. The beaker and contents are then heated on a steam bath to dissolve most of the precipitate. In the phosphotungstates obtained from soybean juices only a small fraction is insoluble in the hot solution. The material is then placed in the refrigerator at from 0° to 5° C. for at least 48 hours. At the end of this time the liquid is decanted off through a paper-pulp pad in a small Büchner funnel into a filter flask under a slight vacuum. The greater share of the precipitate, which remains in the beaker, is stirred up with exactly 10 cc. of cold wash solution, which contains 2.5 grams of 1 to 24 phosphotungstic acid and 3 cc. of concentrated sulfuric acid made up to 100 cc. The washed precipitate is poured on the filter and the wash solution drawn through the slight vacuum.

The filtrate and washings are removed, neutralized to phenolphthalein with 10 *N* sodium hydroxide, made barely acid with glacial acetic acid, and diluted to 35 cc. Samples (20 cc.) are taken for nitrate determinations and 2- to 4-cc. samples for alpha-amino nitrogen.

The precipitate, part of which may remain in the beaker, is dissolved with about 10 cc. of 5 per cent sodium hydroxide and poured on the filter pad. After standing for 4 or 5 minutes (usually a sufficient time to dissolve the entire precipitate) it is drawn into the filter flask by suction. Five cubic centimeters more of 5 per cent sodium hydroxide are added to the filter and allowed to remain there a few minutes. The beaker and filter are then washed well with distilled water, and collected alkaline filtrate and washings (which do not exceed 40 to 45 cc. in volume) are transferred to the semi-micro-Kjeldahl flask, and the nitrogen is determined by either of the procedures described below.

Total Nitrogen in Phosphotungstic Acid Precipitate

The types of compounds precipitated by phosphotungstic acid are notably those which are converted to ammonia only

with difficulty (the presence of the phosphotungstic acid also influences the digestion). A method was described in a previous paper for the rapid semi-microdetermination of total nitrogen (11) with a precision of almost 1 per cent and an accuracy comparable to that of the micro-Kjeldahl. Acid hydrolysis, beyond that normally occurring in the evaporation of water from the dissolved sample, mercury, hydrogen peroxide, phosphoric acid mixtures (7), and combinations of these, as well as combinations with selenium, gave no better results on the basic fraction than selenium alone.

The methods for digestion with sulfuric acid in the Kjeldahl method for the conversion of nitrogenous compounds into ammonia are of two types, depending upon the nature of the material from which the basic precipitate is obtained. In the semi-micromodification of the total nitrogen method to include nitrate in wet samples (11) an alkaline hydrolysis preliminary to digestion is employed. With phosphotungstic acid precipitates from certain materials (notably the soybean) a slight increase in the nitrogen obtained is noted when the preliminary alkaline hydrolysis (omitting Devarda's alloy) is used. On other materials, such as the basic fraction from peptone, no such increase is found. It should be emphasized that the increases found are just below the line of statistical validity. It appears, therefore, that the safest method is to test the material beforehand to determine whether this slight increase on alkaline hydrolysis occurs, before running large numbers of samples by the method. Although the method of alkaline hydrolysis may not generally be of aid, it is given here as procedure II.

PROCEDURE I. The phosphotungstic acid precipitate is dissolved in a slight excess of alkali and transferred to the semi-micro-Kjeldahl flask. Five cubic centimeters of the catalyst-digestion mixture (composed of 2 grams of copper sulfate, 2 grams of selenium oxide, 500 cc. of water, and 500 cc. of concentrated sulfuric acid) are added, evaporated, and digested till white fumes no longer come off and the precipitate has assumed a bright yellow color. After digestion, the contents of the flask are dissolved in water and washed into the aëration tube. The flask is rinsed with 5 per cent sodium hydroxide to dissolve any of the phosphotungstic acid remaining on the sides, and these rinsings are added to the aëration tube. The nitrogen is estimated by aëration as described by Umbreit and Bond (11).

PROCEDURE II. Instead of adding the 5 cc. of catalyst-digestion solution, the flask containing the dissolved phosphotungstates is connected to the Davisson and Parson microtowers (containing 5 cc. of the catalyst-digestion mixture used in I) and heated to boiling, the solution is allowed to suck back, and the towers are washed as earlier described (11). Evaporation, digestion, and estimation of nitrogen proceed as in I.

Although the chemical constitution of the base influences the pH at which it precipitates (10), few data may be found in the literature regarding the influence of variations in acid concentration upon precipitated nitrogen in the extreme acid range. The data in Table I show that in the extreme acid range (from pH 2 to 0) variation in acid concentration produces no significant variation in the nitrogen precipitated by phosphotungstic acid. Similar results were obtained on pure solutions of arginine and histidine. A maximum precipitation was found when the sulfuric acid was present in 5 per cent concentration in agreement with the work of Gulewitsch (4) and Drummond (2), and since subsequent neutralization without too great an increase in volume was possible, 5 per cent sulfuric acid was chosen for the acid concentration of the analytical method.

TABLE I. INFLUENCE OF ACID CONCENTRATION ON NITROGEN PRECIPITATED BY PHOSPHOTUNGSTIC ACID

Material	Sulfuric Acid %	Number of Samples	Nitrogen Found Mg.
Soybean sap	1.8	3	5.25 \pm 0.04
	2.5	3	5.32 \pm 0.08
	5.0	2	5.40 \pm 0.03
	7.0	2	5.12 \pm 0.12

TABLE II. INFLUENCE OF REAGENT CONCENTRATION UPON NITROGEN PRECIPITATED BY PHOSPHOTUNGSTIC ACID FROM SOYBEAN SAP

Concentration of Phosphotungstic Acid Gram	Reagent Cc.	No. of Samples	N Found in Precipitate Mg.
0.1	0.5	1	0.92
0.2	1.0	3	1.67 \pm 0.19
0.3	1.5	2	1.89 \pm 0.14
0.4	2.0	3	1.89 \pm 0.12
0.6	3.0	3	1.83 \pm 0.20

TABLE III. INFLUENCE OF SALT CONCENTRATION ON SOLUBILITY OF PHOSPHOTUNGSTIC ACID PRECIPITATES FROM SOYBEAN SAP

Material	Salt Present %	No. of Samples	Nitrogen in Precipitate Mg.	Nitrogen in Filtrate Mg.
Sap 2, 25 cc.	0	2	2.49 \pm 0.04	0.38 \pm 0.08
	1	3	2.51 \pm 0.06	0.32 \pm 0.10
	2	2	2.46 \pm 0.10	0.33 \pm 0.02
	10	2	2.70 \pm 0.04	0.25 \pm 0.01

Crystallization begins between 2 and 10 per cent.

Barnes and Peters (1) have pointed out that the types of compounds obtained in the precipitate depend upon the phosphotungstic acid used. In this report the acid used was Merck c. p. phosphotungstic acid having a ratio of P_2O_5/WO_3 of 1 to 24, used without further purification.

The data in Table II show that no significant difference is observed due to variation in reagent concentration over the range normally occurring in the analytical procedure as long as there is sufficient reagent to precipitate the basic fraction completely.

Previous workers had indicated (3, 6) that the temperature at which the precipitate was held is a factor in the quantity of nitrogen recovered from various materials. In the case of soybeans the procedure given in the analytical method was found to be satisfactory.

The methods of hydrolysis and aëration used in the general scheme of analysis (9) add a considerable amount of salts (primarily sodium sulfate and acetate) to the solution; the work of Heiduschka and Wolf (5) and Narayana and Sreenivasaya (8) suggests that this might influence the solubility of the precipitate. Van Slyke (12) studied the solubility of the pure diamino acid phosphotungstates at 20° C. and on the assumption that their mutual presence had no effect on the individual solubilities found that 1.16 mg. of nitrogen per 25 cc. were lost through their solubility. Since if the loss through solubility was appreciable or erratic the applicability of a semi-micromethod would be seriously impaired, this point was investigated.

Four hundred cubic centimeters of a normal soybean sap representing the entire plant were rendered peptide-, amide-, and ammonia-free and precipitated under the usual concentration of phosphotungstic acid reagent in 5 per cent sulfuric acid, giving a precipitate very similar to that in analytical samples. Part of the dried precipitate (2.949 grams) was dissolved in barely alkaline water, the solution diluted to 250 cc., and aliquots were taken and precipitated in the usual analytical manner. The data in Table III show that salt concentration has little effect upon the nitrogen found in the precipitate from the sap of the soybean until crystallization begins. The solubility of the composite precipitate was found

to be 0.34 ± 0.02 mg. of nitrogen per 25 cc. (11 samples). Within the limits of experimental error this solubility was found independent of salt concentration (until crystallization begins) and independent of the sap used to prepare the basic material.

PRECISION. The precision of the method was determined by a comparison of duplicates. From Table IV it will be seen that the normal precision is about 0.1 to 0.2 mg. of nitrogen and that the percentages will vary, according to the total amount of nitrogen in the sample.

ACCURACY. The accuracy of the determination may be considered under two problems: (1) the ability to show recovery of basic materials added to the plant juices, and (2) the suitability of the method for estimating the nitrogen found in the basic fraction. Table V shows that the recoveries of arginine-histidine (90 per cent) when added to the hydrolyzed plant sap are within the precision of the method and the recoveries are independent of the nitrogen content of the precipitate.

TABLE IV. PRECISION OF SEMI-MICROMETHOD

No. of Duplicates	Range of Basic Nitrogen Contents	Mean Nitrogen	Difference in Duplicates Av.	%
9	3.53-4.67	4.20	0.17	4.0
18	1.08-2.84	1.96	0.14	7.1
7	0.62-0.94	0.79	0.07	8.8

TABLE V. RECOVERIES OF BASIC NITROGEN ADDED TO SOYBEAN SAP

Material	No. of Samples	N Found in Precipitate	N Corrected for Solubility	Theory %	Recovery %
20 cc. of soybean sap	12	4.29 \pm 0.11	4.63 \pm 0.11
20 cc. of arginine-histidine solution ^{a,b}	12	4.37 \pm 0.08	4.62 \pm 0.08	96.5	..
10 cc. of soybean sap, 10 cc. of arginine-histidine solution ^b	9	4.04 \pm 0.11	4.38 \pm 0.11	94.5	90.0
2 cc. of soybean sap ^c	9	0.72 \pm 0.04	0.86 \pm 0.04
5 cc. of soybean sap	6	2.02 \pm 0.07	2.16 \pm 0.04
5 cc. of arginine solution	8	0.83 \pm 0.03	0.93 \pm 0.03	96.0	..
2 cc. of soybean sap, 5 cc. of arginine solution	9	1.54 \pm 0.08	1.68 \pm 0.08	99.3 ^d	88.4

^a Arginine-histidine solution = 0.24 mg. of nitrogen per cc. (contains 10 per cent of histidine). Solubility of arginine-histidine phosphotungstate = 0.25 \pm 0.03 mg. of nitrogen per 25 cc. (11 samples).

^b Total volume of samples = 25 cc. ^c Total volume per sample = 10 cc. ^d Arginine solution = 0.194 \pm 0.00 mg. of nitrogen per cc. Theoretical value calculated, $0.72 + 0.83 + 0.14$ (for solubility) = 1.69.

Summary

A semi-micromethod for basic nitrogen, estimating basic nitrogen contents of from 2 to 5 mg. of nitrogen with a difference of 5 per cent or less between duplicates, applicable to plant materials is described. The method is independent of reasonable variation in acid concentration, reagent concentration, and salt concentration, but dependent upon preliminary treatment and temperature. Quantitative recoveries of added basic materials were obtained.

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Sodium Hyposulfite Solutions for the Absorption of Oxygen

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THE use of solutions containing sodium hyposulfite, $\text{Na}_2\text{S}_2\text{O}_4$ (or sodium hydrosulfite as it is called commercially), both alone and with the addition of anthraquinone- β -sulfonic acid has been recommended for the absorption of oxygen in gas analysis (3, 5, 9). While working with alkaline solutions of sodium hyposulfite to which anthraquinone- β -sulfonic acid had been added, as suggested by Fieser (5), it was found that if they were used within a day or two of the time they were prepared the rate of absorption was rapid and satisfactory. If, however, the solutions were allowed to stand about for a few days after being made up, even though they had been completely shut off from air, they absorbed oxygen much less rapidly than when freshly prepared, and also tended to become frothy or foamy. Moreover, whether these solutions were used in a packed or bubbler pipet they tended to trap gas. Accordingly, an investigation was made of the sodium hyposulfite solutions recommended by Fieser (5) to find out how effective they were, how their absorptive rate changed with time, and what their capacities were.

Fieser recommends for use in an ordinary pipet a solution made up of 16 grams of sodium hyposulfite, 13.3 grams of sodium hydroxide, and 4 grams of anthraquinone- β -sulfonic acid (procurable from E. I. du Pont de Nemours & Co., Inc., as sodium anthraquinone- β -sulfonate) in 100 cc. of water. This solution was used to absorb the oxygen from air with both an ordinary Orsat pipet and a Francis auto-bubbler pipet. A solution having twice as much caustic was also tried with the bubbler pipet, but the difference in results was negligible. In general, solutions when tested as soon as prepared checked the results of Fieser very well. Fresh solutions took 4 to 5 passes with the Orsat and 3 passes with the bubbler pipet. Thirty seconds were taken in each instance to pass the gas into the pipet. It has since been found more desirable with packed pipets to pass the gas in quickly and leave it there for 15 to 30 seconds. In this way, the gas has a longer time of contact with the packing before the absorbing solution drains off. When the solutions had absorbed about 7 cc. of oxygen per cc. of solution, the number of passes necessary for complete absorption began to increase rapidly, until at the point where 7.5 cc. of oxygen had been absorbed per cc. of solution the latter was practically exhausted. The bubbler pipet took 11 passes for complete absorption of the oxygen in air at this point.

Contrary to the above results, however, if the solutions were tested no more than 3 or 4 days after being made up, gas was trapped so badly, because sodium anthraquinone- β -sulfonate was thrown out of solution when oxygen was absorbed, that their use was not feasible. Such conditions lead to erroneous results. While the sodium anthraquinone- β -sulfonate was gradually reduced again to the soluble form, if left long enough, it involved a period of waiting between each pass to ascertain the true amount of oxygen absorbed. Moreover, such gas-trapping conditions grew rapidly worse with time. Five days after the solutions were prepared, even on waiting for a period of 0.5 to 0.75 hour, the sodium anthraquinone- β -sulfonate was not wholly dissolved, and hence the trapped gas was not wholly removed. This was true in the case of the bubbler pipet as well as the Orsat. Such results indicated that the sodium hyposulfite was no longer functioning with its original potency.

To check the veracity of this supposition, sodium hyposulfite from four different sources was tried with the same results. Then, three lots of solution were made up according to the Fieser formula containing (a) sodium hyposulfite, sodium hydroxide, sodium anthraquinone- β -sulfonate, and water, (b) sodium hyposulfite, sodium hydroxide, and water, and (c) sodium hyposulfite and water. Each solution was divided into two parts, one being set on a shelf in ordinary light, the other wrapped in a towel and shut up in a drawer. All were kept at room temperature. After 10 days the (a) solutions were tested, but in both cases gas trapping and frothing were so bad that the solution was not usable. The same thing was true of the (b) solutions when the correct amount of sodium anthraquinone- β -sulfonate was added. When the correct amounts of sodium anthraquinone- β -sulfonate and caustic were added to the (c) solutions, the sodium anthraquinone- β -sulfonate was not reduced at all. Its reduction would have been obvious because of the deep red shade of the soluble, reduced form. Moreover, the same failure to reduce the sodium anthraquinone- β -sulfonate was observed if solutions of the (b) type were allowed to stand for 15 to 20 days.

These results left little doubt that the failure of the sodium hyposulfite solutions was due to the instability and decomposition of the hyposulfite into products having no reducing ability. Such conclusions have been substantiated by other investigators who used hyposulfite not only in gas analysis but in other fields (1-4, 6-14). Kruse (3, 9) and Ambler (11) found that solutions used for gas analysis became very sluggish on keeping for a couple of weeks. Kruse also reported that such solutions tended to froth. As would be expected, it is generally agreed that the more alkaline the solution the slower the decomposition (2, 6, 13, 14), and the higher the temperature (11, 13, 14) the faster the decomposition. Seyewetz and Kalmar (14) have found the decomposition to be slightly greater in diffuse daylight than in the dark, and somewhat greater still in ultraviolet light.

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Oxidation-Reduction Indicators for Use with Dichromate II

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STRAKA and Oesper (8) found that ethyl sulfate and diphenylamine react to produce a monosulfonate of

$$\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{C}_6\text{H}_5-\text{N}-\text{C}_6\text{H}_4\text{SO}_3\text{Na} \end{array}$$

ethyl diphenylamine, $\text{C}_6\text{H}_5-\text{N}-\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, which can also be produced by the action of ethyl sulfate on ethyl diphenylamine. Though this compound gives a red oxidation product with a trace of dichromate, it has no value as an indicator because a long range of intermediate colors precedes the development of the full red and the attainment of the equivalence point cannot be definitely recognized. However, when diphenylamine was acted on by ethyl sulfate known to be at least 15 years old, an entirely different product resulted—namely, an indicator whose oxidation product was purple, and whose indicator action was satisfactory in all respects (7). Several repetitions have verified these findings, and the present study has shown that the aged ethyl sulfate produced not ethyl diphenylamine monosulfonate,

$$\begin{array}{c} \text{H} \\ | \\ \text{C}_6\text{H}_5-\text{N}-\text{C}_6\text{H}_4\text{SO}_3\text{Na} \end{array}$$

but a diphenylamine monosulfonate, $\text{C}_6\text{H}_5-\text{N}-\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ (found, sodium, 8.43 per cent; sulfur, 11.37; calculated, sodium, 8.49 per cent; sulfur, 11.48).

This striking difference led to a search for the ingredient of the old ethyl sulfate that so markedly influenced the course of the reaction. The old ethyl sulfate was dark, rather viscous, and smelled strongly of sulfur dioxide. Tests for heavy metals were negative. Ordinary ethyl sulfate was artificially aged by heating it on a boiling water bath for 24 hours, another sample was boiled at atmospheric pressure for 5 minutes, and other samples were deliberately contaminated with ethyl hydrogen sulfate, sulfuric acid, ethyl sulfite, butyl sulfate, iodine, and lead, ferric, copper, and mercuric sulfates, but runs with samples containing these likely catalysts or decomposition products of ethyl sulfate gave in every case a product identical with that produced by ordinary ethyl sulfate, and the determining factor is still to be discovered.

Experimental

Since ordinary ethyl sulfate leads to no satisfactory product, and since aged ethyl sulfate is obviously not constantly available, a higher homolog of ethyl sulfate, *n*-butyl sulfate, was made to react with diphenylamine in the hope of producing a usable indicator.

Twenty-one grams (0.1 mole) of *n*-dibutyl sulfate (1) and 16.9 grams (0.1 mole) of diphenylamine were heated together on a boiling water bath for 1 hour, and then on a metal bath at 130° to 140° C. for 1 hour. A solution of sodium ethylate (4.8 grams of sodium in 200 ml. of ethanol) was then added and refluxed until the dark tarry reaction mass became white. The alcohol was distilled off, the residue taken up in water and filtered, and the filtrate thoroughly extracted with ether to remove any residual diphenylamine. The water layer was warmed and air bubbled through it until the ether was removed. Concentrated sodium hydroxide solution was added cautiously until a faint turbidity appeared. The desired sodium salt precipitates slowly, and after 24 hours the suspension was filtered, the salt sucked as dry as possible, redissolved in warm ethyl alcohol, and precipitated by an excess of ether. This treatment removes most of the alkali. The purification is completed by dissolving the salt in warm alcohol, passing in carbon dioxide until no more

sodium carbonate separates, and concentrating the filtrate on the water bath to incipient crystallization.

The sodium salt obtained from this procedure contains 8.35 per cent of sodium and 11.42 per cent of sulfur, corresponding to diphenylamine monosodium sulfonate. It gives the same color on oxidation as does the product from old ethyl sulfate; in fact the two products are identical. This was definitely proved by preparing the *p*-toluidine salt of each (3); after two recrystallizations from water, the derivatives individually not only melted sharply at the same temperature (196–197° C.) but a mixture gave the same melting point.

$$\begin{array}{c} \text{H} \\ | \\ \text{C}_6\text{H}_5-\text{N}-\text{C}_6\text{H}_4\text{SO}_3\text{Na} \end{array}$$

This indicator, $\text{C}_6\text{H}_5-\text{N}-\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, gives a deep purple with a slight excess of oxidizing agent. The color is stable for at least 15 minutes and is sharply discharged by a slight excess of ferrous ion, etc. Mercury salts do not inhibit its indicator properties. Four to 5 drops of 0.1 per cent water solution are ample in volumes not exceeding 400 ml. Fifteen to 25 ml. of the ordinary sulfuric-phosphoric acid retarder solution are essential to satisfactory functioning. Comparative analyses of a series of chromium and iron ores demonstrated that this internal indicator is fully as reliable as ferricyanide. The indicator allowance, comparing with ferricyanide, does not exceed 0.1 ml. using 0.1 *N* dichromate, and if the latter is standardized against ores of known iron or chromium content, the indicator error is negligible.

Straka and Oesper found that *m*-tolylphenylamine and *p*-tolylphenylamine are satisfactory indicators, provided mercury salts are absent. The present writers have carried *o*-, *m*-, and *p*-tolylphenylamine through the reaction with ethyl sulfate, using the procedure described above. The products contained 8.21, 8.19, and 8.22 per cent of sodium,

$$\begin{array}{c} \text{H} \\ | \\ \text{C}_6\text{H}_5-\text{N}-\text{C}_6\text{H}_3\text{CH}_3\text{SO}_3\text{Na} \end{array}$$

respectively, corresponding to $\text{C}_6\text{H}_5-\text{N}-\text{C}_6\text{H}_3\text{CH}_3\text{SO}_3\text{Na}$, which contains 8.09 per cent of sodium. The meta and para compounds show no indicator properties, but the *o*-tolylphenylamine monosodium sulfonate, whose oxidation product is deep red, is a satisfactory indicator, provided there is not more hydrochloric acid present than corresponds to 2 to 3 ml. of specific gravity 1.18 per 250 ml. of solution. Mercuric, mercurous, and stannic salts do not interfere, and sulfuric acid may be present in any reasonable concentrations without harm.

In view of the sulfonating properties of ethyl sulfate, it was tried on diphenyl benzidine with the hope of producing a soluble sulfonate. Ten grams of diphenyl benzidine (6) and 24 ml. of ethyl sulfate were refluxed for 5 hours in xylene solution and then refluxed with a solution of 8.5 grams of sodium in 300 ml. of ethanol. The light gray product was dried, ground, extracted with xylene, and then dissolved in ethanol. The sodium salt after purification contained 5.40 per cent of sodium, corresponding to diphenyl benzidine monosulfonate which contains 5.25 per cent of sodium. This is a satisfactory indicator, giving a red color with excess oxidizing agent, but in this instance also erratic results are obtained if more than low concentrations of hydrochloric acid are present.

The following compounds were found to give colored oxidation products, but the color changes are not striking enough to warrant the use of the materials as oxidation-reduction indicators: *N,N'*-dimethyl benzidine (9), benzidine monosulfonic acid (2), and dinaphthocarbazon (5).

The very excellent indicator prepared by Straka and Oesper from the reaction of ethyl sulfate on acetyl diphenylamine has now been purified by the procedure described above. Analysis shows it to be a monosulfonate of diphenylamine: sodium found, 8.46 per cent; calculated, 8.49. No less than three monosulfonated derivatives of diphenylamine have now been recommended for use as oxidation-reduction indicators: (1) that of Kolthoff and Sarver (4); (2) that of Straka and Oesper; and (3) that produced by aged ethyl sulfate or, better, butyl sulfate and diphenylamine. They

are probably isomers or mixtures of isomers, a point that will be studied in the continuation of this effort to find new and possibly better indicators for use with dichromate.

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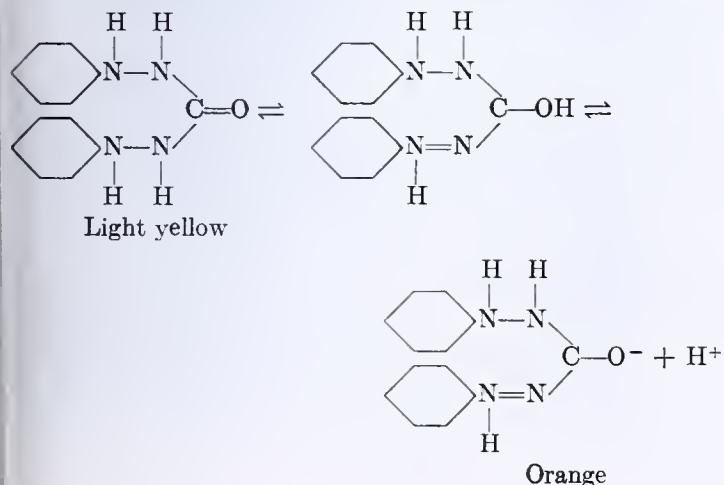
Titration of Chloride Ion with Mercuric Nitrate Solutions

Using Diphenyl Carbazide Indicator

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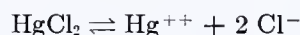
DIPHENYL carbazide and diphenyl carbazone have been suggested as indicators in the titration of chloride with mercuric nitrate solutions by Dubsy and Trtilek (1, 2, 3, 10) and by Slotta and Muller (9) in place of the inaccurate Mohr and inconvenient Volhard methods (6). The method depends upon the formation, from mercuric ion and the indicator, of a deep blue-violet complex, after the chloride ions have combined to form slightly ionized mercuric chloride. Unexplained anomalous effects of acidity on the sensitivity and absolute values given by the titration were found, which make their results unreproducible. The author has found that both precision and accuracy can be obtained if the proper precautions are taken, and that mercuric oxide, first used as a primary standard in alkalimetry (5, 7), may be conveniently used as a primary standard in preparing mercuric nitrate solutions.

The probable mechanism of this titration may be seen from a few qualitative observations. Diphenyl carbazide is an acid-base indicator, changing from a light yellow in acid solution to a deep orange in alkaline solution, in the pH range 6.6 to 7.4 (determined with phosphate-citrate buffers). The equilibrium is probably of the following type:



In alkaline, neutral, or slightly acid solution, dilute mercuric chloride gives the deep blue-violet color with the indicator. If a solution containing both mercuric chloride and diphenyl carbazide is just above pH 7, the addition of large amounts of potassium chloride will not remove the color, whereas a drop of nitric acid will. On the other hand, with a highly acid solution containing the indicator, such as 1 to 1 nitric acid, a large amount of mercuric nitrate must be added before any color is seen.

These observations seem to indicate that it is only the alkaline form of the indicator which forms the deep blue-violet complex with mercuric ion. As the acidity of the solution increases, the above equilibrium is driven to the left and the concentration of the alkaline form decreases, so that beyond a certain acidity we may expect the sensitivity of the titration to be too low for great precision. Also, that mercuric chloride itself gives the blue-violet color with the indicator in weakly acid solution is probably due to the fact that, at low acidity, the concentration of the alkaline form of the indicator is great enough to give appreciable reaction with mercuric ion from the dissociation of mercuric chloride:



We may then expect that at low acidities the end point will come too soon, giving low values in the titration. Evidence supporting these statements is given below.

Materials and Solutions

Potassium Chloride. The recrystallized material was used in preparing a standard 0.1 *N* solution.

Diphenyl Carbazide and Diphenyl Carbazone. Colorless Eastman Kodak diphenyl carbazide (m. p., 167.5°, cor.) was used directly. Diphenyl carbazone was prepared by the method of Heller (4) and showed after three recrystallizations from acetone and water a melting point of 149.5° to 150° (cor.). Although this melting point is 8° lower than that of Heller or of Slotta and Jacobi (8), further recrystallizations from benzene or from benzene and petroleum ether failed to raise it. (This is of little significance, since the indicator solution used probably contains both the carbazide and the carbazone.)

A saturated solution of diphenyl carbazide in 95 per cent ethyl alcohol, which gradually turns red after standing for several days, was used as the indicator. No difference in action could be detected between this solution, a fresh solution of the carbazide, and a diphenyl carbazone solution in alcohol.

Sodium Hydroxide. Standard 0.1 *N* and 0.025 *N* solutions were prepared and stored by the usual methods.

Hydrochloric Acid. A standard 0.1 *N* solution was prepared from constant-boiling hydrochloric acid.

0.20 *N* Nitric Acid.

Mercuric Oxide. c. p. mercuric oxide was dissolved in 1 to 1 nitric acid and filtered. To the filtrate was added 8 *M* sodium hydroxide until precipitation was complete. The precipitate was filtered and washed free from alkali (phenolphthalein). The yellow mercuric oxide was then dried over phosphorus pentoxide for 10 days, during which period it was powdered from time to time.

Mercuric Nitrate Solutions. In preparing the 0.1 *N* and 0.025 *N* solutions, as little nitric acid as possible was used. After the required amount of mercuric oxide was weighed accurately and suspended in water, the calculated equivalent amount of nitric acid was added. Then to the well-stirred mixture, concentrated nitric acid was added drop by drop until complete solution took place. After making up to volume, the solutions were no more than 0.01 *N* with respect to nitric acid.

Titration Procedures

With 0.1 *N* mercuric nitrate the following procedure has been found satisfactory:

The final volume of the solution being titrated should be about 80 to 100 cc. If the chloride solution to be titrated is acid, it should first be neutralized with sodium hydroxide. If the acid titer is also required, 5 drops of diphenyl carbazide are added and the solution is titrated with standard sodium hydroxide to the orange color. Four cubic centimeters of 0.2 *N* nitric acid are added and the solution is then titrated with 0.1 *N* mercuric nitrate. About 5 drops before the end point, a pink-violet color begins to develop; at the end point, one drop changes the color from a light violet to a deep blue-violet.

Theoretically the blank should correct not only for the 4 cc. of nitric acid added, but also for the amount of nitric acid present in the mercuric nitrate used in the titration. Actually the error involved in neglecting this last factor is less than 0.02 cc. of 0.1 *N* mercuric nitrate, if the amount of nitric acid in the mercuric nitrate solution is less than 0.01 *N*.

With 0.025 *N* mercuric nitrate additional precautions must be taken:

The final volume of the solution being titrated in this case should be 65 ± 10 cc. If the chloride solution to be titrated is acid, 2 drops of 0.2 per cent bromophenol blue are added, and the solution is titrated with standard sodium hydroxide to the full blue color. Four cubic centimeters of 0.2 *N* nitric acid are added, then 5 drops of diphenyl carbazide indicator, and the solution is titrated with 0.025 *N* mercuric nitrate to a definite pink color, which can be reproduced to ±0.02 cc., with the aid of a daylight lamp. The yellow color imparted by the bromophenol blue in no way interferes with the mercuric nitrate end point, and to make conditions uniform for all experiments presented here, 2 drops of bromophenol blue are added to all titration mixtures where 0.025 *N* mercuric nitrate is used.

The blank correction is determined not only with 2 drops of 0.2 per cent bromophenol blue and 4 cc. of nitric acid, but also with nitric acid equivalent to the amount of acid in the mercuric nitrate used in the titration. Neglecting the latter may cause as much as 0.07 cc. error in the blank.

The experiments listed in Table I, where the acidity was being varied, may be divided into 2 groups:

In Nos. 1 to 3, most of the mercuric nitrate used had to be first neutralized, while in Nos. 4 to 8 no such neutralization was necessary. Nos. 1 to 3 were performed by pipetting 5.020 ± 0.005 cc. of 0.1052₄ *N* potassium chloride and running in 20.00 cc. of 0.02455 *N* mercuric nitrate. The acid was then titrated with 0.025 *N* sodium hydroxide to bromophenol blue, the specified amount of nitric acid and 5 drops of diphenyl carbazide were added, and the mercuric nitrate titration was completed. In

Nos. 4 to 8, to the 5 cc. of potassium chloride were added 2 drops of bromophenol blue, the specified amount of nitric acid, and 5 drops of diphenyl carbazide. The solution was then titrated with mercuric nitrate.

An accurate determination of the acidity of a mercuric nitrate solution may be made by the sodium hydroxide titration mentioned just above. Mercuric oxide will not precipitate during the titration with alkali if an excess of chloride ion is present and if the solution is dilute.

Discussion of Results

The accuracy obtainable by this method is shown by comparative results obtained by titration of 0.1 *N* hydrochloric acid and 0.1 *N* potassium chloride with 0.1074₂ *N* mercuric nitrate, and by other methods. The accuracy is never poorer than 0.3 per cent.

Concentration of KCl		
From weight of KCl used		0.1052 ₄ <i>N</i>
From Hg(NO ₃) ₂ titration		0.1050 ₂ <i>N</i>
Concentration of HCl		
From NaOH titration		0.1042 ₆ <i>N</i>
From Hg(NO ₃) ₂ titration		0.1043 ₃ <i>N</i>

The effect of acidity on the titration can be seen in Table I. The titer given in the third column is the mean of two values never deviating by more than 0.04 cc. except in No. 8. The blank was determined for the total amount of nitric acid from the two sources. It is obvious, upon comparison of the final corrected titer with the calculated value of 21.52 cc., that above pH 2.0 the titers are all too low, as expected from the discussion above. The agreement is good in the range 1.5 to 2.0. Below pH 1.5, the sensitivity and the precision are both lowered; the results, however, are invariably correct within the reduced precision at these acidities, when the blank correction is applied. In the pH range 1.5 to 7.0, the end point is sharp whether or not the absolute value of the titer is correct.

TABLE I. EFFECT OF ACIDITY ON TITRATION
(Titration of 5.020 cc. of 0.1052₄ *N* KCl with 0.02455 *N* Hg(NO₃)₂;^a
calculated titer = 21.52 cc.)

No.	0.2 <i>N</i> HNO ₃ Added Cc.	pH ^b	Titer Cc.	HNO ₃ Blank	Titer (Cor.) Cc.
1	0.35	2.9	20.76	0.01	20.75
2	0.70	2.6	21.11	0.01	21.10
3	1.2	2.4	21.30	0.02	21.28
4	2.0	2.0	21.53	0.06	21.47
5	3.0	1.9	21.60	0.10	21.50
6	4.0	1.8	21.66	0.15	21.51
7	6.0	1.7	21.76	0.22	21.54
8	10.0	1.5	21.90	0.36	21.54

^a This mercuric nitrate solution was 0.0078 *N* with respect to nitric acid.

^b Calculated from the nitric acid added to the titration mixture from the two sources.

These pH values are significant only for the titration conditions described here. Variation in the volume of the solution being titrated and in the amount of indicator used will probably shift the optimum pH range through displacement of the various equilibria described above.

According to the theory of the titration presented here, an increase in the concentration of mercuric chloride present should probably decrease the titer. This has been found to be true, but titration of varying amounts of potassium chloride (1 to 10 cc. of 0.1 *N* potassium chloride) using from 5 to 45 cc. of mercuric nitrate (0.025 *N*) on the buret, shows a maximum error of 0.2 per cent due to this effect.

The titration has already been applied successfully in determination of iodide (2) and silver (3). It has been used in this laboratory to determine mercuric ion in dilute solution. This is done by adding a known amount of chloride (excess), titrating the acid to a bromophenol blue end point, adjusting the acidity, and titrating with mercuric nitrate to a diphenyl carbazide end point.

Acknowledgment

The author is grateful to L. P. Hammett for his interest and helpful suggestions throughout this research.

Summary

The titration of chloride ion with mercuric nitrate solution using diphenyl carbazide indicator has been found to give accurate results in a definite range of acidity. A probable explanation is given. Mercuric oxide may be used as a primary standard in the preparation of mercuric nitrate solutions. With the method given above, the accuracy of the method is better than 0.3 per cent with ordinary volumetric apparatus.

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Special Head for Kjeldahl Distillation Apparatus

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UNITS for Kjeldahl distillations usually are so constructed as to require a glass connecting bulb of some description to connect the flask with the condensing apparatus. Theoretically this setup is all that can be desired, since the connecting bulb holds back any spray from the boiling liquid and breaks up any foaming which may occur. However, the flasks have nothing to hold them securely in place other than a rubber connection at the top, and most distillations of this kind do some bumping.

Figure 1 shows a modified Kjeldahl distillation apparatus which has been successfully used in this laboratory. It consists of a well-known manufactured unit with the addition of special metal heads to take the place of the usual glass connecting bulbs. Figure 2 is a cross section of the head and is self-explanatory. The block-tin condenser tube which comes with this particular apparatus is the right length to be soldered into the head and should extend to within 2 or 3 mm. of the top (soldered cap). These heads are held securely in place by a strip of wood 32 mm. (1.25 inches) wide, sawed off longitudinally through the centers of the 32-mm. (1.25-inch) holes in which the heads are placed. A long screw between each two heads and at the ends holds them securely in position after they are adjusted properly for height. The wire gauze and glass beads completely break up and return to the flask any spray or foam which may occur.

The operation of the unit is very simple: The rubber

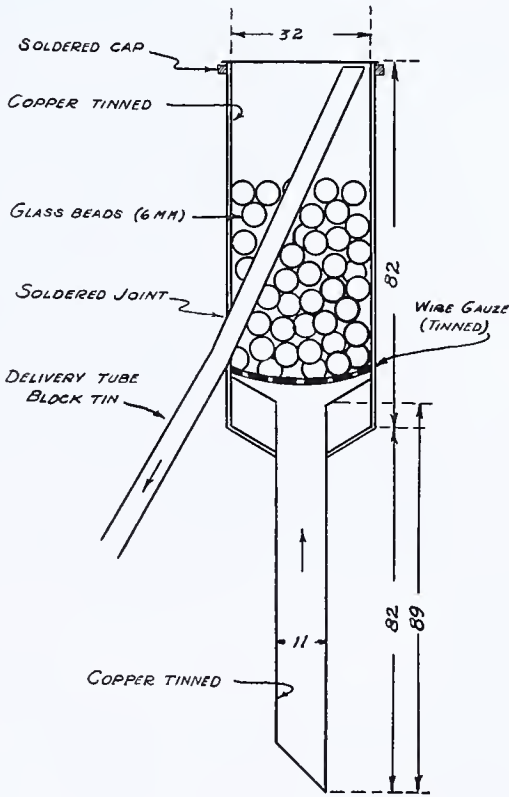


FIGURE 2. KJELDAHL DISTILLATION HEAD
(All dimensions in millimeters)

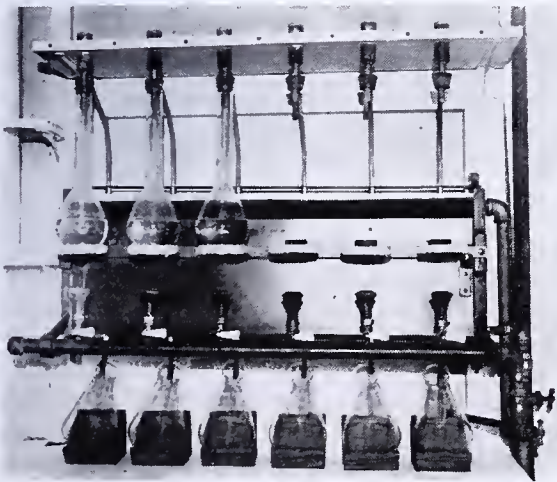


FIGURE 1. MODIFIED KJELDAHL DISTILLATION APPARATUS

stopper is pushed to the top of the lower tube, the 800-cc. Kjeldahl flask put in position, and the stopper pushed down with a twist into the neck of the flask, holding it tightly.

Figure 1 also shows supports for the receiving flasks which are very convenient, especially in adjusting the delivery tubes to the proper depth in the acid. If these tubes are made sufficiently large (inverted filter tubes serve nicely) and are kept just under the surface of the acid, there will be no danger of acid sucking up into the condensers because of uneven heating.

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Determination of Gold in Dental Gold Alloys

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THE present method was devised to shorten the time required for the accurate determination of gold in dental gold alloys. The chief components of sixty of these alloys analyzed by the author are gold, silver, copper, platinum, and palladium. Small amounts of iridium, probably present in the platinum used, have been encountered. The base metals noted in addition to copper were nickel, zinc, tin, and indium.

The general basis of the author's procedure is the excellent scheme of analysis developed by Swanger (1). Gold is precipitated by sulfur dioxide after the removal of silver, iridium, and tin. In the presence of platinum and palladium appreciable quantities of these metals are carried down with gold, and a reprecipitation of the latter with oxalic acid is necessary (2). This step in itself requires a minimum of 4 hours, and it was with a view of shortening this part of the procedure that the present method was devised.

A search for a reagent that would satisfactorily precipitate gold alone in the presence of platinum and palladium resulted in the selection of tetraethylammonium chloride. This substance is regularly listed in the Synthetic Organic Chemicals Catalog of the Eastman Kodak Company. An aqueous solution of the salt yields with auric gold a difficultly soluble canary-yellow precipitate that is found to be free from platinum and palladium when the precipitation is made in the presence of salts of these two metals. It was hoped that the precipitate could be washed, dried, and then weighed directly for the determination of gold. However, losses occurred during washing with water or with alcohol, and it was found necessary to wash with a 15 per cent aqueous solution of the reagent. Furthermore, analyses showed that the precipitate was not of ideal composition, and could only be approximately expressed as two molecules of tetraethylammonium chloride for each molecule of auric chloride.

With direct weighing out of the question, ignition of the precipitate to metallic gold was attempted. This was found to be inadvisable, since frothing resulted in a loss of material even at the relatively low temperature necessary for the decomposition of the compound. A satisfactory procedure was arrived at by the use of a reducing agent on the precipitated gold compound. W. M. Lauer of this university suggested the use of glucose, and it was found by the author that a hot alkaline 20 per cent aqueous solution brought about rapid reduction to metallic gold. Mirrors were not formed, the metal settled rapidly and presented no difficulties in filtering.

Detailed Procedure for Analysis

About 0.5 to 0.7 gram of a dental alloy is dissolved in aqua regia. The solution is freed from silver, iridium, and tin, and then the gold is precipitated with sulfur dioxide. These steps are all carried out according to the directions given by Swanger (3). The precipitated gold is filtered off, washed thoroughly with hot 1 per cent hydrochloric acid, and then dissolved in 20 cc. of dilute aqua regia. The paper pulp is filtered off and washed with hot 1 per cent hydrochloric acid. The filtrate is boiled down to a volume of from 2 to 3 cc. and after the addition of 5 cc. of concentrated hydrochloric acid the solution is again evaporated to a volume of about 3 cc. Water is added to bring the volume up to 20 cc. (10 cc. if the amount of gold present is less than 10 mg.), and then a 15 per cent aqueous solution of tetraethylammonium chloride is added. For each 0.1 gram of the sample 4 cc. of the reagent solution should be added.

The yellow precipitate formed is allowed to settle for 15 minutes. It is then filtered off on a paper of the grade of Schleicher and Schüll No. 589, Blue Ribbon, and washed four times with 5-cc. portions of the 15 per cent solution of the reagent. The filtrate contains any platinum and palladium carried down with the gold during the sulfur dioxide precipitation. Paper and precipitate are transferred to a beaker and covered with 35 cc. of a freshly

prepared 20 per cent aqueous glucose solution to which 2 grams of sodium hydroxide have been added. After boiling for 1 minute an equal volume of water is added. The liquid is then decanted from the filter paper and metallic gold, being poured through a filter to retain any small particles of gold that may be suspended in the liquid. Filter paper and metallic gold remaining in the beaker are boiled with 25 cc. of concentrated hydrochloric acid until the paper is disintegrated. An equal volume of water is added and the paper pulp and gold are filtered off onto the same paper through which the decanted liquid had been poured. After thorough washing with hot water and then preliminary drying at 120° C., paper and gold are ignited in a porcelain crucible. The above procedure can be carried to completion within a period of 3 hours after the beginning of the precipitation of the gold with sulfur dioxide.

As stated above, the filtrate from the tetraethylammonium chloride precipitation of the gold contains any platinum and palladium carried down during the original sulfur dioxide precipitation. These small amounts of platinum and palladium are recovered as sulfides in the usual way, then dissolved in aqua regia and returned to the main portion of the solution containing these and other components of the alloy. This portion of the analysis can be resumed in approximately 2 hours after the beginning of the sulfur dioxide precipitation of gold. When oxalic acid is used to separate gold from small amounts of platinum and palladium, the determination of these metals, copper, and others such as nickel and zinc cannot be carried forward until from 6 to 7 hours after the beginning of the sulfur dioxide precipitation of gold.

Accuracy of Gold Determination

Table I shows the results of determinations made by the present method on solutions containing known amounts of gold, platinum, and palladium.

TABLE I. RESULTS OF DETERMINATIONS

Solution	Au, Pt, and Pd in Each Solution			Au, Pt, and Pd Found by Analysis		
	Au	Pt	Pd	Au	Pt	Pd
	Gram	Gram	Gram	Gram	Gram	Gram
1	0.2006	0.0020	0.0020	0.1997	0.0020	0.0019
2	0.2006	0.0040	0.0033	0.2002	0.0039	0.0034
3	0.1003	0.1000	0.0830	0.1001	0.1004	0.0833
4	0.0020	0.1000	0.0830	0.0020	0.1002	0.0832
5	0.0020	0.2000	0.1660	0.0019	0.2003	0.1664

Since Swanger has made a series of determinations showing the amount of platinum and palladium carried down with gold in the sulfur dioxide precipitation (2), it was not deemed necessary to repeat this work in all determinations made by the present method. Table II shows the amount of contamination of gold in a series of three determinations.

TABLE II. CONTAMINATION OF GOLD

Au, Pt, and Pd in Each Sample			Pt and Pd Recovered from Filtrate of Tetraethylammonium Chloride Precipitation of Au	
			Pt	Pd
Au	Pt	Pd	Gram	Gram
Gram	Gram	Gram		
0.0010	0.1025	0.0002
0.1000	0.1025	0.1020	0.0023	0.0027
0.2000	0.0021	0.0020	0.0003	0.0004

It will be seen from Table III, showing the results of analyses of typical dental alloys, that the present method compares favorably with the sulfur dioxide-oxalic acid method for the determination of gold in the presence of platinum and palladium. Each alloy was analyzed by the present method and by the procedure worked out by Swanger. With the exception of the values given for gold, the percentages listed represent the average value of two determinations.

The cost of the tetraethylammonium chloride used in the determination is based upon a price of \$6.00 per 100 grams quoted in Eastman Organic Chemicals List No. 26, April, 1935. For a 0.7-gram sample, the largest used by the author

TABLE III. ANALYSES OF DENTAL ALLOYS

Alloy No.	Ag %	Pd %	Cu %	Pt %	Ni %	Zn %	Au by SO ₂ and H ₂ C ₂ O ₄ %	Total %	Au by Et ₄ NCl %
1	9.16	...	8.98	2.38	1.95	1.39	76.06	99.92	75.99
2	25.59	3.89	8.49	2.49	59.24	99.70	59.69
3	9.41	11.45	8.77	0.37	..	1.54	68.56	100.10	68.49
4	43.77	22.23	13.71	2.97	17.23	99.91	17.41
5	16.75	4.15	22.85	56.32	100.07	56.68
6	45.19	3.99	..	0.59	49.96	99.73	50.12
7 ^a	44.02	28.02	14.02	1.55	11.16	99.80	11.21
8 ^b	15.46	...	14.14	2.76	..	4.99	60.34	99.85	60.69

^a Contains 1.03% indium.
^b Contains 2.16% tin.

monium chloride as a reagent for gold. Tetraethylammonium chloride quantitatively precipitates gold in the presence of small amounts of platinum and palladium carried down with gold that has been precipitated by sulfur dioxide.

Acknowledgment

The author wishes to acknowledge the courtesy shown by Kenneth Casselman of the W. E. Mowrey Company, St. Paul, Minn., in furnishing all the alloys used in the pursuit of this research.

in the analysis of any dental gold alloy, a total of 48 cc. of the 15 per cent aqueous solution of the reagent is required. This brings the reagent cost to \$0.37. Against this cost, however, may be set up the very considerable saving in time involved.

Summary

The time required for the determination of gold in dental gold alloys is materially shortened by the use of tetraethylam-

Literature Cited

- (1) Swanger, W. H., Bur. Standards, *Sci. Paper* 532 (1926).

(2) *Ibid.*, pp. 225-6.

(3) *Ibid.*, pp. 217-27.
- RECEIVED July 28, 1934. Resubmitted April 13, 1936. Presented in part before the Division of Physical and Inorganic Chemistry at the 87th Meeting of the American Chemical Society, St. Petersburg, Fla., March 26 to 30, 1934.

Bactericidal Value of Coal-Tar Disinfectants

Limitations of the *B. Typhosus* Phenol Coefficient as a Measure

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ALTHOUGH it has been customary for many years to describe the potency of germicides in terms of phenol coefficients, nevertheless it is not at all unusual to find that this term is still being used with an incomplete realization of its significance. It is overlooked that when used without any other qualifications, it refers to one microorganism only, *B. typhosus*. It is assumed, often by erroneous implication, that the germicidal effect upon other pathogenic microorganisms corresponds to that upon *B. typhosus*—i. e., that a disinfectant with a phenol coefficient of 10 for instance, is ten times more potent than phenol, not only with respect to *B. typhosus*, but to all other pathogenic microorganisms as well.

There exist certain quantitative relationships in the effects of a number of germicides upon different pathogenic microorganisms, of such a character that from the observed action upon *B. typhosus* it is possible to draw a conclusion concerning the probable action upon other microorganisms; but there are other instances in which any such relation is completely lacking. The following discussion will be limited to disinfectants of coal-tar origin, because the statement of germicidal potency in terms of phenol coefficient is, or should be, restricted to this class of products, by a more or less common agreement.

It is not intended to give a detailed review of preceding publications which deal with the limitations involved in any at-

tempted interpretation of the germicidal potency of disinfectants on the basis of their *B. typhosus* phenol coefficients alone (2, 6). However, considerable study has been devoted to this subject by previous investigators.

Two Groups of Coal-Tar Disinfectants

Although the term "coal-tar disinfectants" is often used in a general sense, it is important to remember that there are two different groups of products falling under this classification, each with very definite characteristics—viz., the cresylic and the tar-oil groups. The former comprises preparations containing as active principle phenol derivatives of low molecular weight, such as the isomeric cresols and xylenols; the cresol compound of the U. S. Pharmacopœia is the outstanding example of this class. The products of the latter group contain, in addition to phenolic constituents, varying proportions of coal-tar hydrocarbons, mostly mono- and dimethylnaphthalenes, which are derived from the so-called neutral oil. Soaps made from vegetable oils or resins form an essential part of the formulas of both groups, their miscibility with water being due to the presence of soap. Physically, the two classes may be distinguished by the appearance of their mixtures with water; in low concentrations, the cresylic disinfectants form practically clear aqueous solutions, while those of the tar-oil group show a milky turbidity.

The phenol coefficient which is used extensively as a yardstick of the germicidal potency, not only of pure phenol derivatives but also of technical coal-tar disinfectants, is not of itself satisfactory for this purpose. In the former case it becomes inoperative with compounds of higher molecular weight, in the latter it tends to give an exaggerated picture of the germicidal potency of certain so-called emulsifiable or tar-oil disinfectants, owing to the presence of naphthalene hydrocarbons, although being more definitive in the case of the cresylic disinfectants. The determination of a supplementary *Streptococcus* phenol coefficient, in addition to the established *B. typhosus* phenol coefficient, would prevent incorrect ideas concerning the general germicidal potency of certain disinfectants, arising from a consideration of their *B. typhosus* phenol coefficients alone.

TABLE I. GERMICIDAL ACTION OF *p*-ALKYLPHENYL DERIVATIVES AT 37° C.

	<i>B. typhosus</i>		<i>Staph. aureus</i>		<i>M. tuberculosis (hom.)</i>		<i>Monilia albicans</i>	
	Concen- tration ^a	Phenol coeffi- cient	Concen- tration ^a	Phenol coeffi- cient	Concen- tration ^a	Phenol coeffi- cient	Concen- tration ^a	Phenol coeffi- cient
Phenol	1:150-160	1.0	1:70-80	1.0	1:90-100	1.0	1:90-100	1.0
2-Methyl	1:350	2.3	1:160	2.3	1:200	2.0	1:200	2.0
3-Methyl	1:350	2.3	1:160	2.3	1:200	2.0	1:200	2.0
4-Methyl	1:350	2.3	1:160	2.3	1:200	2.0	1:200	2.0
4-Ethyl	1:1000	6.3	1:500	6.3	1:600	6.7	1:700	7.8
2,4-Dimethyl	1:800	5.0	1:350	4.4	1:400	4.0	1:500	5.0
2,5-Dimethyl	1:800	5.0	1:350	4.4	1:400	4.0	1:400	4.0
3,4-Dimethyl	1:800	5.0	1:300	3.8	1:400	4.0	1:400	4.0
2,6-Dimethyl	1:600	3.8	1:350	4.4	1:400	4.0	1:350	3.5
4- <i>n</i> -Propyl	1:2750	18.3	1:1300	16.3	1:1600	17.8	1:1600	17.8
4- <i>n</i> -Butyl	1:7000	46.7	1:3500	43.7	1:4000	44.4	1:4000	44.4
4- <i>n</i> -Amyl	1:8000	53.3	1:10,000	125.0	1:12,000	133.0	1:14,000	156.0
4- <i>tert</i> -Amyl	1:4500	30.0	1:7500	93.8	1:10,000	111.1	1:10,000	100.0
4- <i>n</i> -Hexyl	1:5000	33.3	1:25,000	313.0	1:35,000	389.0	1:30,000	333.0
4- <i>n</i> -Heptyl	(1:2500)	(16.7)	1:50,000	625.0	1:60,000	667.0	1:50,000	556.0

^a Minimum concentrations effective in 10 minutes.

Germicidal Action of Phenol Homologs

Before discussing the relationship between the composition of the various technical coal-tar disinfectants and their action upon different pathogenic microorganisms, it is well to consider the pertinent conditions obtaining in the case of definite phenol homologs. Table I gives the quantitative results obtained with *B. typhosus*, *Staphylococcus aureus*, *Mycobacterium tuberculosis (hom.)*, and *Monilia albicans* (3). The consideration of the minimum germicidal concentrations and of the phenol coefficients calculated therefrom discloses that in this series the germicidal potency with regard to all four test organisms increases with the increasing molecular weight until the amyl derivative is reached; beginning with this point, the further increase of the molecular weight produces a very considerable increase of the germicidal action upon *Staphylococcus aureus*, *Mycobacterium tuberculosis (hom.)*, and *Monilia albicans*, while with respect to *B. typhosus* their effect drops, becoming rather indefinite in the case of the heptylphenol, which nevertheless shows considerable efficacy against the other three test organisms. The figures indicate that in the case of the compounds up to and including butylphenol, the *B. typhosus* phenol coefficient might serve as a reasonably accurate index of germicidal potency, since a compound which is, for example, 2, 6, 18, or 45 times, respectively, more effective than phenol against *B. typhosus*, is also approximately as many times more effective against the other vegetative microorganisms. However, beginning with the amyl compound, this relation ceases to exist; in this case, as well as in that of the higher homologs, the *B. typhosus* phenol coefficient is no longer an index of the general germicidal efficacy.

While it is not claimed, of course, that all the normal alkylphenols listed in Table I occur in coal-tar disinfectants or in disinfectants made from tar acids, the conditions found in this series of homologous phenol derivatives are referred to in order to demonstrate the existence of certain functional relationships between the chemical constitution and germicidal action. However, attention is called to the results obtained with the pure cresols and xylenols (methyl and dimethyl phenols) given in Table I and also in Table II in which the parallelism in the germicidal effects upon different microorganisms is distinctly evident. These results are significant, particularly because cresols and xylenols occur in the usual run of coal-tar disinfectants. (The experimental conditions of the tests described in Tables I and II differ, in that in the former case the temperature at which the culture was exposed to the action of the disinfectant solution was 37° C., in the latter 20° C.)

It may be mentioned in passing that the term "quasi-specific" has been proposed previously by the authors to describe the effect such as that shown by *n*-heptylphenol which

is extremely active against *Staphylococcus aureus* and yet little effective against *B. typhosus*.

Effect of Technical Coal-Tar Disinfectants

In applying these findings to the usual variety of cresylic disinfectants, which as a rule contain the cresol and xylene isomers, the *B. typhosus* phenol coefficient may be expected to give a reasonable idea of their general germicidal potency. This is borne out by the results obtained with certain commercial cresylic disinfectants of different germicidal strengths listed in the first part of Table III.

Table III gives in its second part the results obtained with six commercial tar-oil disinfectants, and here the picture is entirely different. Although the preparations are listed in the order of their *B. typhosus* phenol coefficient, beginning with the lowest figure, there is no regularity in the relationship between the *B. typhosus* phenol coefficient and the phenol coefficients obtained with the other microorganisms. By way of comparison with the disinfectants of the cresylic group, where the ratio of the *B. typhosus* and *Streptococcus* phenol coefficients, for example, is not in excess of approximately 2 to 1 for any given product, in the tar-oil group there occur such ratios as 8 to 1 or even 20 to 1.

A comparison of the germicidal effects upon *B. typhosus* and *Streptococcus hemolyticus* of a number of technical tar-oil and cresylic disinfectants was reported recently by Philbrick (4). His findings substantiate the contention that the *B. typhosus* phenol coefficient is unable to furnish an adequate description of the germicidal potency of coal-tar disinfectants. This author lists certain products whose comparatively high *B. typhosus* phenol coefficients of over 3 would conceal the fact that they are from about ten to thirty times less effective against *Streptococcus hemolyticus*, thus tending to misrepresent their germicidal value. Reference is made in this connection also to the very instructive paper by Brewer and Ruehle (1) in which a considerable number of similar phenol coefficient relationships (with *B. typhosus* and *Staphylococcus aureus*) are given for both the tar-oil and the cresylic disinfectants.

Neutral Oil in Emulsifiable or Tar-Oil Disinfectants

The domestic tar-oil disinfectants contain varying proportions of "neutral oil," consisting mostly of methyl- and dimethylnaphthalenes, besides other hydrocarbons (fluorene, acenaphthene), organic bases (quinoline, pyridine) and their alkyl derivatives, certain oxygenated compounds, organic sulfur compounds, etc. Neutral oil contains practically no phenol or phenol derivatives. Obviously, therefore, the anti-bacterial action of disinfectants containing considerable proportions of neutral oil hydrocarbons cannot be expected to show the functional regularity encountered in the case of phenolic germicides. Few systematic data are available concerning the anti-bacterial properties of neutral oil, or its effect as an admixture to phenolic germicides.

In an effort to obtain further information on this subject, the authors prepared and tested saponaceous (linseed-oil soap) mixtures of U. S. P. cresol with neutral oil containing various proportions of these two constituents. Admittedly, such mixtures are not entirely representative of the composition of the technical tar-oil disinfectants, but there is enough resemblance to justify their use in a systematic in-

TABLE II. GERMICIDAL ACTION OF CRESOLS AND XYLENOLS AT 20° C.

	<i>B. typhosus</i>		<i>B. dysenteriae</i> (Flexner)		<i>Staph. aureus</i>		<i>Streptococcus</i> (hemol.)		<i>M. tuberculosis</i>		<i>Trichophyton rosaceum</i>	
	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.
Phenol	1:80-90	1.0	1:90-100	1.0	1:60	1.0	1:60	1.0	1:60	1.0	1:80	1.0
2-Methyl	1:200	2.5	1:250	2.5	1:130	2.2	1:150	2.5	1:160	2.7	1:160	2.0
3-Methyl	1:200	2.5	1:200	2.0	1:140	2.3	1:140	2.3	1:140	2.3	1:160	2.0
4-Methyl	1:200	2.5	1:200	2.0	1:130	2.2	1:140	2.3	1:140	2.3	1:160	2.0
2,5-Dimethyl	1:400	5.0	1:500	5.5	1:250	4.2	1:250	4.2	1:300	5.0	1:300	3.8
2,4-Dimethyl	1:400	5.0	1:500	5.5	1:250	4.2	1:300	5.0	1:350	5.0	1:350	4.4
3,4-Dimethyl	1:400	5.0	1:500	5.5	1:250	4.2	1:250	4.2	1:300	5.0	1:300	3.8
2,6-Dimethyl	1:400	5.0	1:500	5.5	1:250	4.2	1:300	5.0	1:300	5.0	1:300	3.8

^a Minimum concentrations effective in 10 minutes.

TABLE III. GERMICIDAL ACTION OF CERTAIN CRESYLIC AND TAR-OIL DISINFECTANTS

	Temperature 20° C.											
	<i>B. typhosus</i>		<i>B. dysenteriae</i> (Flexner)		<i>Streptococcus</i> (hemol.)		<i>Staph. aureus</i>		<i>M. tuberculosis</i> (hom.)		<i>Trichophyton rosaceum</i>	
	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.
Cresol compound, U. S. P.	1:200	2.3	1:200	2.2	1:100	1.4	1:100	1.6	1:140	2.3	1:70	1.0
Cresylic disinfectant I	1:300	3.8	1:400	4.4	1:180	2.6	1:120	2.4	1:200	3.3	1:160	2.3
Cresylic disinfectant II	1:500	5.5	1:500	5.5	1:200	2.9	1:180	3.0	1:300	5.0	1:300	4.3
Tar-oil disinfectant I	1:300	2.8	1:350	3.9	1:50	0.7	1:40	0.7	1:400	2.3	1:35	0.5
Tar-oil disinfectant II	1:600	6.7	1:600	6.7	1:25	0.4	1:25	0.4	1:160	2.7	1:40	0.5
Tar-oil disinfectant III	1:700	7.8	1:500	5.5	1:25	0.4	1:25	0.4	1:140	2.3	1:40	0.5
Tar-oil disinfectant IV	1:700	8.8	1:600	6.7	1:70	1.0	1:40	0.7	1:160	2.7	1:50	0.71
Tar-oil disinfectant V	1:800	8.8	1:1000	11.1	1:120	1.7	1:100	1.7	1:80	1.3	1:100	1.4
Tar-oil disinfectant VI	1:1000	11.1	1:1000	11.1	1:120	1.7	1:120	2.0	1:250	4.2	1:100	1.4
Phenol (control)	1:80-90	1.0	1:90-100	1.0	1:60-70	1.0	1:60	1.0	1:60	1.0	1:80	1.0

^a Minimum concentrations effective in 10 minutes.

TABLE IV. GERMICIDAL ACTION OF SAPONAGEOUS MIXTURES OF U. S. P. CRESOL AND NEUTRAL OIL AT 20° C.

		<i>B. typhosus</i>		<i>B. dysenteriae</i> (Flexner)		<i>Streptococcus</i> (hemol.)		<i>Staph. aureus</i>		<i>M. tuberculosis</i>		<i>Trichophyton rosaceum</i>	
		Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.	Concn. ^a	Phenol coeff.
U. S. P. cresol	50%	1:160	2.0	1:200	2.0	1:100	1.7	1:90	1.5	1:160	2.7	1:80	1.0
U. S. P. cresol	40%	1:300	3.8	1:300	3.0	1:100	1.7	1:120	2.0	1:250	4.2	1:100	1.3
Neutral oil	10%												
U. S. P. cresol	30%	1:350	4.4	1:300	3.3	1:70	1.2	1:60	1.0	1:200	3.3	1:80	1.0
Neutral oil	20%												
U. S. P. cresol	20%	1:300 [*]	3.8	1:300	3.3	(1:40)	(0.67)	1:40	0.67	1:120	2.0	1:40	0.5
Neutral oil	30%												
U. S. P. cresol	10%	1:250	3.1	1:200	2.2	(1:6)	(0.1)	(1:5)	(0.08)	1:100	1.7	1:8	1.0
Neutral oil	40%												
Neutral oil	50%	1:160	2.0	1:160	1.6	1:6	0.08	1:5	0.08	1:16	0.27	1:5	0.06
High-boiling tar acids	50%	1:1000	12.5	1:1000	11.1	1:350	5.8	1:400	6.7	1:400	6.7	1:300	3.8
Phenol (control)		1:80-90	1.0	1:90-100	1.0	1:60	1.0	1:60	1.0	1:60	1.0	1:80	1.0

^a Minimum concentrations effective in 10 minutes.

vestigation of this matter. Table IV lists the results obtained (at 20° C.). It will be noted that an increasing proportion of neutral oil at first brings about an apparent increase in the effect upon *B. typhosus*, the phenol coefficient of the disinfectant mixture consisting of 30 per cent of U. S. P. cresol and 20 per cent of neutral oil, being more than twice that of the preparation containing 50 per cent of U. S. P. cresol. The further increase in the proportion of neutral oil lowers the *B. typhosus* phenol coefficient, although this figure never drops below that of the product with 50 per cent of U. S. P. cresol. Indeed, an emulsion corresponding to a neutral oil content of 50 per cent appears to produce the same effect upon *B. typhosus* as a 50 per cent cresol preparation.

But this effect upon *B. typhosus* is not descriptive of the action upon other test organisms. *B. dysenteriae*, which is related to *B. typhosus*, resembles the latter in its resistance to these mixtures. However, the other test organisms studied—viz., *Streptococcus hemolyticus*, *Mycobacterium tuberculosis*, and *Trichophyton rosaceum*—do not follow the course of *B. typhosus*; here the gradual replacement of U. S. P. cresol by neutral oil causes a gradual decrease in the germicidal potency of such mixtures. Thus, here is another significant instance of the inability of the *B. typhosus* phenol coefficient to describe the general germicidal potency of a disinfectant; the discrepancy between the effects upon *B. typhosus* (and *B. dysenteriae*) on one hand, and upon *Streptococcus*, *Staphylococcus*, *Mycobacterium tuberculosis*, and

Trichophyton rosaceum on the other, is strongly in evidence, as illustrated, for instance, by a comparison of the effects of the 50 per cent cresol preparation with one containing 10 per cent of cresol and 40 per cent of neutral oil. In the case of the mixture containing neutral oil only, a consideration of the *B. typhosus* phenol coefficient alone might lead one to assume that this mixture has the same germicidal potency as that containing cresol only. Yet the results obtained with the other test organisms disclose the vast germicidal superiority of the cresol mixture.

In order to prove that no other constituents of neutral oil except α - and β -methylnaphthalene play any significant role in producing this phenomenon, several experiments were run in which these naphthalene derivatives were mixed with U. S. P. cresol, and emulsified in the same manner as the mixtures of cresol and neutral oil. Table V states the experimental results in detail; they appear to agree entirely with those obtained in the case of the cresol-*N*-neutral oil mixtures dealt with in Table IV, thus showing conclusively that the methylnaphthalenes, which constitute the bulk of neutral oil, are responsible for the apparent quasi-specific enhancement of the germicidal potency of tar-oil disinfectants with respect to *B. typhosus*.

By way of interest, Table V gives also the results obtained with a disinfectant containing 50 per cent of high-boiling tar acids derived from a foreign blast-furnace tar. This disinfectant shows a very favorable germicidal potency with respect to all test organisms used.

TABLE V. GERMICIDAL ACTION OF SAPONACEOUS MIXTURES OF U. S. P. CRESOL WITH α - AND β -METHYLNAPHTHALENE AT 20° C.

	α -Methylnaphthalene				β -Methylnaphthalene			
	<i>B. typhosus</i>	<i>Streptococcus</i>	<i>M. tuberculosis</i>	<i>Trichophyton rosaceum</i>	<i>B. typhosus</i>	<i>Streptococcus</i>	<i>M. tuberculosis</i>	<i>Trichophyton rosaceum</i>
	Phenol coeff. ^a	Concn. ^a	Phenol coeff.	Phenol coeff.	Phenol coeff.	Concn. ^a	Phenol coeff.	Phenol coeff.
U. S. P. cresol 40%-methylnaphthalene 10%	1:350	1:120	2.0	1.3	1:350	1:120	2.0	1:100
U. S. P. cresol 25%-methylnaphthalene 25%	1:300	1:80	1.3	0.6	1:350	1:80	1.3	1:100
U. S. P. cresol 10%-methylnaphthalene 40%	1:300	1:10	0.2	0.13	1:300	1:200	3.3	1:40
Methylnaphthalene 50%	1:200	(1:5)	(0.08)	<0.06

^a Minimum concentrations effective in 10 minutes.

Conclusion

Although the *B. typhosus* phenol coefficient is used extensively as an index of the germicidal potency of coal-tar disinfectants, it is deemed desirable at this time to restate its limitations in the light of some newer experimental data. In the case of the pure alkyl-phenol derivatives, the germicidal effect upon *B. typhosus* of the lower homologs parallels that upon other vegetative pathogenic microorganisms to such an extent that the *B. typhosus* phenol coefficient might be regarded as a relative measure of the germicidal potency of these compounds. Since cresylic disinfectants contain some lower phenol homologs as the active principle, the same consideration would apply in their case.

In the case of the emulsifiable or tar-oil disinfectants, however, there exists no quantitative relationship between the effect upon *B. typhosus* and that upon other microorganisms; thus, some disinfectants of this type, with high *B. typhosus* phenol coefficients, may be less effective against other pathogenic microorganisms than those with lower *B. typhosus* coefficients; or of two products with the same phenol coefficient, one may be a better general germicide than the other. This condition arises mainly from the indefiniteness of the composition of the tar-oil disinfectants, and more particularly from the variations in the ratio of phenolic to nonphenolic constituents. The latter, consisting mostly of naphthalene hydrocarbons, appear to have a specific effect upon *B. typhosus* and certain related bacteria, such as *B. dysenteriae*, but are much less effective, or practically ineffective, against other pathogenic microorganisms.

So-Called 5 Per Cent Safety Factor

It has been customary to require that the concentration of a given preparation to be applied in disinfection correspond in its effect upon *B. typhosus* to a 5 per cent phenol solution. (Such a concentration is calculated simply by

multiplying the *B. typhosus* phenol coefficient by 20.) While there is hardly any question as to the arbitrary character of this requirement, it may be assumed that its author made it in the belief that a solution of this strength would be germicidal to other pathogenic microorganisms of epidemiologic significance. The results of Tables III and IV indicate, however, that such a solution will not always be germicidal—e. g., to a resistant streptococcus culture when tested by a laboratory method—even though it is possible that under certain conditions, such as in the disinfection of walls, floors, etc., a dilution arrived at in this fashion may be sufficient for the purpose in question.

A consideration of this 5 per cent phenol safety factor, however, bears no relation whatever to the problem of a bacteriological evaluation of germicides. This is emphasized particularly because of the insistence of some authors upon the relevance of this arbitrary figure in the bacteriological evaluation of germicides, although the issue is primarily one of specificity (or quasi-specificity) versus nonspecificity.

Recommendation

Since, therefore, a delineation of the bactericidal value of every coal-tar disinfectant cannot be achieved on the basis of its *B. typhosus* phenol coefficient alone, the regulatory requirement of some additional statement as to the germicidal potency with respect to a representative microorganism, other than *B. typhosus*, appears to be desirable. The hemolytic streptococcus is an infectious microorganism, and some strains appear to lend themselves for cultivation in the laboratory so as to show under standard testing conditions a standard resistance to phenol. Moreover, since the susceptibility to the action of coal-tar disinfectants of a resistant hemolytic streptococcus strain bears a quantitative resemblance to that of other microorganisms, whose destruction should be aimed at in the practice of disinfection, the adoption of a supplementary *Streptococcus hemolyticus* phenol coefficient is recommended. The consideration of both the *B. typhosus* and the *Streptococcus hemolyticus* phenol coefficients would supply a much more accurate and complete picture of the germicidal potency than that of the *B. typhosus* phenol coefficient alone. It would aid also in preventing misconceptions as to the germicidal potency of those products whose high *B. typhosus* phenol coefficients are not descriptive of their germicidal potency with regard to other microorganisms.

Experimental Notes

All tests involving the use of *B. typhosus* and *Staphylococcus aureus* were carried out according to the F. D. A. technic (5). As to the details of technic used in tests with the other microorganisms, the paper by Klarmann, Shternov, and Gates (3) should be consulted.

Acknowledgment

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The Application of Statistics to Quantitative Analysis

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IT IS GENERALLY recognized that the results of any scientific investigation must prove reproducible. Likewise the value of an analytical procedure is based on the expectation that it may be used at any future time with the success claimed by its author. Therefore, it is only proper to measure the merit of an analytical method in terms of the certainty, or probability, with which its successful reproduction can be predicted (11). The data required for such a prediction are obtained by the use of the methods of statistics that are customary in the evaluation of physical measurements and in the discussion of determinations of atomic weight. A simple outline is here presented for the organization of analytical research and the presentation of its results, which will be helpful in the establishment of the precision and accuracy of proposed methods.

Precision and Accuracy

Only numbers derived from definitions are exactly known and can be given with as many significant figures as desired; measured quantities are known only within the limits of the methods used for their determination.

The effect of accidental and of constant errors is demonstrated in Figure 1, which shows the results of four series of determinations plotted as abscissas; the arithmetical mean of each series is indicated by a vertical line. It is assumed that four different methods have been used for the determinations of the quantity. In series I and II the accidental errors are small and the results in either series agree closely among themselves; methods I and II show a high degree of precision. With methods III and IV the accidental errors are large and the results in either series do not show satisfactory agreement; methods III and IV have a low degree of precision. It is obvious that such methods of low precision are highly impractical, since only the mean of a large number of determinations could be of any use. On the other hand methods I and II will give satisfactory results in practical application, though with method II allowance has to be made for the constant error which appears as the difference, "truth" minus arithmetical mean.

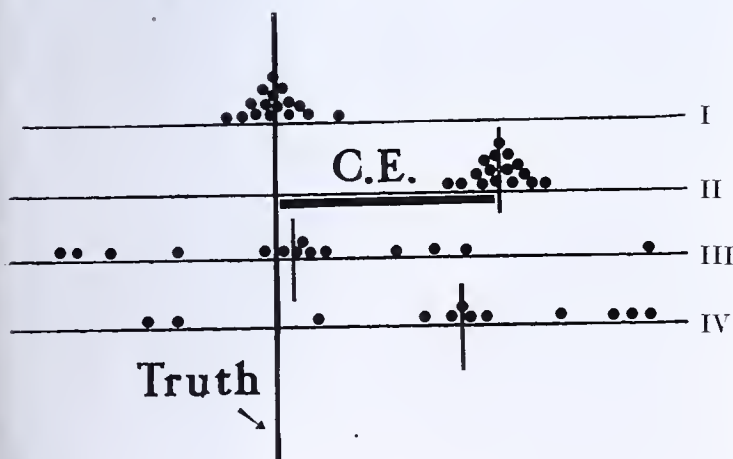


FIGURE 1. EFFECT OF ACCIDENTAL AND CONSTANT ERRORS

The purpose of the calibration of a method is the determination of its constant error. The precision of the constant error depends upon the precision with which the arithmetical mean and the expected result (truth) are known (Table IV).

The calibration of a method is carried out by its repeated application to the determination of quantities known by the use of other reliable methods. Thus the calibration estab-

lishes not only the accuracy related to the constant error, but also the precision determined by the accidental errors of the method. The results of such a set of determinations will never check exactly, if the determinations are carried out to the full delicacy of which the procedure is capable. The best representative value of the discordant set of figures is its arithmetical mean, provided that the results have been obtained under the same conditions and are equally trustworthy (12). The proof rests upon the fact that the positive and negative deviations, being equally probable, will ultimately balance each other (13), thus clearing the arithmetical mean more or less from the influence of the accidental errors. Accordingly, the discussion of the result of a series of determinations should be based on the arithmetical mean and its precision.

TABLE I. ASH DETERMINATIONS ON POTASSIUM SULFATE AND AZOBENZENE

No.	Ash %	Arithmetical Mean %	$\pm a_m$ %
1	53.4		
2	53.1	53.25	0.10
3	52.7	53.07	0.14
4	52.8	53.00	0.13
5	52.7	52.94	0.11
6	52.5	52.87	0.11
7	53.5	52.96	0.12
8	52.8	52.95	0.11
9	53.0	52.94	0.10

One should not rely on the mean of a small number of observations which, by accident, may agree closely and furnish an arithmetical mean of apparently high precision. The author met with an interesting example of the malice of chance in a study on the precision of sampling, in which ash determinations were carried out on 1- to 3-mg. samples of a solid mixture of potassium sulfate and azobenzene. In Table I the results are listed in the exact order in which they were obtained. The first six determinations seemed to indicate the presence of a time factor, as the ash content of the mixture appeared to decrease continuously. Absorption of moisture by the mixture offered a possible explanation. Finally the seventh determination proved the accidental nature of this remarkable series of results.

A survey of Table I shows that the arithmetical mean does not become sufficiently constant within the first six determinations to be trustworthy. Also the precision of the mean, a_m , is unreliable when the mean is derived from too small a number of observations; in Table I the mean of the first two determinations seems to possess the same precision as the mean of the whole series. Considering everything, it appears proper to require at least four to ten determinations in every set of analyses carried out for the calibration of a method (8, 13); the number of determinations in a series may be decreased according to the amount of available preliminary information on the precision of the method.

As a measure of precision, the average deviation is suggested (8), since it is an appropriate standard of comparison when attention is directed to the relative precision in different series of observations. Furthermore, the average deviation furnishes useful information even when the presence of (unknown) constant errors renders a further application of the theory of errors of questionable utility, because it will allow us to compare the magnitude of the constant errors

affecting different series of observations, and so lead to their discovery and elimination (13).

If n is the number of determinations and d_1, d_2, d_n represent the absolute deviations of the individual results from the arithmetical mean, Q , the average deviations are calculated as follows:

Absolute average deviation of a single determination,	$a_s = \pm \frac{(d_1) + (d_2) + \dots (d_n)}{n}$
Relative average deviation of a single determination,	$a_s' = \pm \frac{1000 a_s}{Q} \text{ } \%$
Absolute average deviation of the arithmetical mean,	$a_m = \pm \frac{a_s}{\sqrt{n}}$
Relative average deviation of the arithmetical mean,	$a_m' = \pm \frac{1000 a_m}{Q} \text{ } \%$

The absolute precisions have the same dimension as the determined quantity, Q ; the relative precisions are expressed in parts per thousand to avoid confusion with the results of quantitative analyses which are usually reported in parts per cent (8).

Reports on sets of determinations for the calibration of a method may be reduced to listing the number of determinations, the arithmetical mean of the results, the absolute average deviation of the mean, and finally the relative average deviation of the mean. Thus the table in the report on the calibration of the microdetermination of aluminum by weighing the hydroxyquinolate (3) could have been reduced to the statement: The calibration was carried out with samples of 1.7 to 6.5 mg. of pure $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The arithmetical mean of nine determinations gave 10.79 ± 0.011 per cent Al_2O_3 ($\pm 1 \text{ } \%$); 10.77 per cent expected.

This statement not only has the advantage of brevity, but conveys information which cannot be obtained from the tabulation of the results without calculation. The original figures are not made available, but the customary presentation in table form does not list the figures of the original weighings and buret readings. Furthermore, in presentation in table form one will often be forced to list only part of the results obtained, which leads to a very undesirable selection of the material which in itself constitutes a misrepresentation of facts. On the other hand, the arithmetical mean must include all the results of the series. Inconsistent results can be excluded only if it is definitely proved that the discrepancy is due to a digression (mistake, accident) from the standard procedure used in the calibration. Otherwise such results, if not included in the calculation of the mean, must be separately reported.

As to the immediate information obtainable from the mean and its precision, the probability that in the future an error will occur, which is larger than four times the average deviation, is approximately one in a thousand. This means that a repetition of the calibration of the microdetermination of aluminum will probably give a result between 10.83 and 10.75 per cent of alumina. As the expected result, 10.77 per cent, lies within this range, the presence of a constant error cannot be justly assumed. The calibration was actually repeated in a different location, with different apparatus and reagents by another worker (5), and the arithmetical mean of a series of fourteen determinations was 10.78 ± 0.006 per cent Al_2O_3 ($\pm 0.6 \text{ } \%$).

In this second series the aluminum determinations were carried out from solutions containing various concentrations of beryllium. The close agreement of the means proves that the presence of beryllium has no disturbing influence on the determination of the aluminum. The slightly better precision of the second series may be due to the fact that the first series was carried out by seven different experimenters (thus

including the variation of the personal errors), whereas the second series was performed by one person.

The average deviations of a single determination are obtained from the abbreviated report by multiplying the average deviations of the mean by \sqrt{n} :

$$a_s = \pm 0.033 \text{ } \% \text{ } \text{Al}_2\text{O}_3 \text{ } (a_s' = \pm 3 \text{ } \%)$$

The a_s' indicates that in future application of the method an individual determination will give on an average a deviation of $\pm 3 \text{ } \%$ from the expected value, and will hardly ever show a deviation of more than $\pm 12 \text{ } \%$ from the truth. When predicting the precision of the arithmetical mean of m future determinations, the above precisions for the individual determination are to be divided by \sqrt{m} .

However, all these predictions hold only if future determinations are carried out under conditions identical with those under which the calibration was performed. Such an exact duplication of the experiment by another person is possible only if the procedure of the calibration is carefully and completely reported. In general the description should include the technic, the material, form, and dimensions of apparatus, and the purity specifications, concentrations, and volumes of the reagents. Usually the description must be the more elaborate, the greater the precision and accuracy of the method. Of course, the development of the proposed method should be sufficiently complete to exclude unnecessary restrictions and precautions. Just as a maze of directions indicates insufficient knowledge of the processes involved, a general disregard of cookbook procedures indicates a woeful misconception of the fundamental principles of experimental work. The degree by which the standardization of a procedure must sometimes be extended to meet the requirements of an increased sensitivity can be demonstrated in the determination of the precision of balances.

The precision of an analytical balance is determined by repeating a weighing six to ten times in a series and by calculating the average deviation of a single weighing, a_s , from the set of results. If the balance is only arrested and released between consecutive weighings, nothing but the soundness of the balance construction is tested. In order to obtain the conditions of an actual weighing, it is necessary to lift off the rider after arresting the balance, to move the rider carrier sideways, and then to replace the rider as exactly as possible in the original position before proceeding to the next weighing. The determination of the precision should be carried out with various loads on the pans, and the precaution may be taken to shift slightly the positions of the weights on the pans between the weighings. Further specifications appear superfluous when considering the precision of balances for analytical routine work which requires weighings to 0.1 mg.

The precision of inexpensive analytical balances, used by students for 3 to 4 years, has been determined in this way (Table II). A 5-mg. rider is used with these balances. The precision ± 0.16 mg. was observed under extreme conditions which should be avoided in actual weighing; the 100-gram weights were placed in different positions so near the edges of the pans that the pan arrests made contact on the opposite side of the circumference of the pans. One hundred grams is the maximum permissible load for these balances.

TABLE II. PRECISION OF BALANCES

	Precision, $\pm a_s$		
	No. 4764 Mg.	No. 4751 Mg.	No. 2288 Mg.
Zero load, rider not touched	0.005	0.007	0.031
Zero load, rider operated	0.005	0.008	0.023
100-gram load, rider operated	0.076
100-gram weights near edge of pans	0.16

In microchemical work the attempt is made to reproduce weighings with a precision of a few thousandths of a milligram. No matter whether a precision (analytical) balance, an assay balance, or a microchemical balance of the Kuhlmann type is

used for this work, the following additional factors must be carefully considered in the development of a standard procedure of weighing (16):

1. Special attention must be paid to the position of the rider and to imperfections of the rider scale.
2. Special care must be taken to prevent setting up a temperature gradient in the balance. A variation of the arm lengths of the beam, as well as the formation of convection currents in the case, is to be avoided.
3. The temperature coefficient of balances becomes noticeable in weighings of high precision. A variation of the temperature affects not only the zero reading but also the weighings to an amount which varies with the load and cannot be exactly calculated. In addition the effects of temperature changes show a marked time lag. To avoid these difficulties, the balance room must be kept at constant temperature, and the experimenter must reduce the duration of his stays in front of the balance to a minimum.
4. If changes of barometric pressure are likely to occur between consecutive weighings, the variations of the buoyant effect must be considered.
5. Special care must be devoted to the perfect functioning of the arresting mechanism and to its proper use. Electrostatic charges not only occur on the objects weighed, but also may happen on the agate surfaces of the balance construction and cause a phenomenon similar to the sticking of the arresting contacts.
6. Displacements of the zero reading may be caused by deposition of dust on the various parts of the balance construction.

The history of the use of the microchemical balance (the term "microchemical balance" was originated by Pregl and refers only to balances of the Kuhlmann type) is proof not only of the difficulties encountered in the attempt to increase the sensitivity of the analytical balance, but also of the disregard of the principles of physical measurements. A state of confusion was brought about by incompletely, or not at all, reporting the conditions under which the various accuracies had been observed. Thus Pregl's original claim (15) of a precision of ± 0.001 mg. refers to the mean of a series of weighings, carried out in rapid succession with a load of a fraction of a gram, and possibly without touching the rider between the weighings. Even under these conditions the quoted precision can be attained only in the absence of a disturbance of the equilibrium of the balance by the body temperature of the observer. With greater load the precision of the microchemical balance shows a noticeable decrease. If the weighings are taken at greater time intervals, changes of room temperature and of barometric pressure may cause variations up to 0.1 mg. As a matter of fact, whereas the precision of an analytical balance can be established within one hour, the investigation of Schwarz-Bergkampff (16) had to be extended over more than half a year in order to give sufficient information on the efficiency of the microchemical balance.

Calibration of Chemical Procedures

The calibration of chemical procedures for the determination of constant errors is carried out by the performance of control analyses with known quantities of the constituent to be determined or detected; controls, run with zero quantities of this constituent, are called blanks, and in general will give information about interfering matter introduced by the reagents and apparatus. The results of blanks may contradict those of controls. Since controls are carried out under conditions more similar to those of actual analyses, they are better suited for the determination of constant errors (14). Under all conditions, the calibration should be carried out in such a way as to permit establishment of the precision as well as the determination of constant errors.

The different effects of additive and proportional constant errors can be seen from Table III, which summarizes the results of calibrations carried out in connection with an at-

tempt to develop a micromethod for the determination of aluminum with the use of alumina as weighing form (4). Pure $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was used in the controls. The solutions of alum were first treated with a constant volume of hydrochloric acid to obtain a standard concentration of ammonium salt. Following this, the solutions were made slightly alkaline with ammonia for the precipitation of the aluminum hydroxide.

A blank indicated purity of the reagents, since the negligible increase of the weight of the crucible was accounted for by the weight of the ash of the filter paper. The results of controls with increasing quantities of alum are listed in the second column of Table III. The fact that determinations on small quantities of alum showed a greater deviation from the truth than those on large quantities indicated the presence of an additive constant error, which was caused by co-precipitation of the silicic acid introduced with the ammonia. The constancy of the amount of silicic acid was explained by the fact that the major part of the ammonia was required for the neutralization of the constant amount of hydrochloric acid added in all determinations. The silica content of the precipitates was determined by treating the precipitates with hydrofluoric acid. The corrected results in the third column of Table III agree rather well with the expected results. The ability of aluminum hydroxide to carry down silicic acid is well known. Of course, with blanks the silicic acid remains in solution, because of the absence of a solid phase able to co-precipitate the silica.

TABLE III. DETERMINATION OF ALUMINUM AS Al_2O_3

$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ Taken Grams	With Use of NH_3 from Stock Bottle Corrected for -0.021 g. SiO_2		NH_3 Freshly Distilled, Al_2O_3 Found Gram
	Al_2O_3 found Gram	Gram	
1.0000	1×0.1288	1×0.1078	1×0.1087
2.0000	2×0.1192	2×0.1087	2×0.1089
3.0000	3×0.1163	3×0.1093	3×0.1086
4.0000	4×0.1147	4×0.1094	4×0.1088
Expected:	$n \times 0.1077$	Arithmetical mean = $10.875 \pm 0.005\%$ Al_2O_3	

The results obtained with the use of freshly distilled ammonia (fourth column Table III) are not in very good agreement with the theoretical Al_2O_3 content of alum; on the average they are 10 % too high. The presence of a constant error is indicated by the fact that the arithmetical mean of a new series of determinations is expected to fall in the range of 10.85 to 10.90 per cent of Al_2O_3 , which does not include the expected value 10.77 per cent. The good agreement of the results of analyses with varying quantities of sample indicates the presence of a proportional constant error. The same error was discovered by Hahn (10) when he tried to check the weights of aluminum hydroxyquinolate precipitates against the weights of alumina obtained from identical samples of pure aluminum metal. Also Fresenius (9) must have observed the high results obtained with the use of alumina as weighing form. The alumina is extremely hygroscopic (6); even when it has been ignited in a platinum crucible over a blast lamp, it will have absorbed from 1 to 2 per cent of water when it is ready for weighing. The water content of the weighed oxide was directly determined (4) by ignition in a sealed tube, centrifuging the condensate into a fine capillary, and measuring the volume of the liquid.

In additional experiments it was found that with pure Al_2O_3 , ignition over the blast lamp is indispensable for the reduction of the degree of hygroscopicity to the above-mentioned amount, while with mixtures of aluminum and ferric oxides the use of somewhat lower temperatures would be permissible. The idea of using alumina as a weighing form in microanalysis was finally abandoned, since no crucible material is available which shows a sufficient constancy of

weight when heated above 900° C. The aluminum hydroxyquinolate is by far a superior weighing form, as it has all of the properties which seem especially desirable in micro-analysis: The precipitate consists of relatively large crystals which are easy to filter and to wash; treatment previous to weighing does not require temperatures above 800° C. (drying at 140° C. suffices); and the weighing form has a large molecular weight.

The above example illustrates the different effects of additive and proportional constant errors. In the case of the former, the absolute error (+0.021 gram of SiO₂) and, with the latter, the relative error (+10 % of water) are constant. Additive errors are usually caused by impurities of reagents added in constant quantities, by the solubility of the precipitate in a constant volume of solution, by the excess reagent required to produce the indicator change, or by the losses or gains determined by the constant surface area of apparatus. Proportional errors may be due to basing the calculation on a wrongly assumed composition of the weighing form, to incomplete reactions, or to faulty calibration of measuring apparatus (weights, balance, burets, pipets, volumetric flasks). Additive errors may become proportional errors, or vice versa, depending on the procedure adopted in a series of experiments. Likewise the terms "constant" and "accidental" cannot be assigned without reference to special conditions. The deviations introduced by the impurities of a reagent appear as accidental if the reagent is used in varying quantities, whereas the use of a definite amount of reagent will produce a constant error. When a series of analyses has been carried out by one person, the personal factor must be regarded as a constant error and will result in a definite deviation from the truth. If the analyses of a series are carried out by a number of people, the personal errors become accidental in nature; they will affect the precision of the arithmetical mean, but will not cause a definite digression from its expected value.

In conclusion, progressing standardization will tend to convert accidental errors into constant errors, thus increasing the precision. Calibration allows the correction of the results of precise determinations for constant errors and thus improves the accuracy.

Propagation of Errors

The final result of a quantitative analysis is usually derived from the combination of several measurements. For the calculation the following general formula can be used, in which the result, R , appears as a function of the measured quantity, M , the chemical factor, f , the amount of sample, S , and the capacities, C_1, C_2, C_3 , of the volumetric flasks and c_1, c_2, c_3 of the pipets used in taking aliquot parts:

$$R = 100 \frac{fM}{S} \frac{C_1 C_2 C_3}{c_1 c_2 c_3} \quad (1)$$

Depending on whether fM and S are both expressed in weight or volume, the result, R , is obtained in per cent by weight or by volume; if fM is expressed in grams and S has been measured in milliliters, the result is in grams per 100 ml. The meanings of f and M are interpreted according to the method in use. In gravimetric analysis, M is the weight of the "weighing form" and f is the fraction of the equivalent weight of the reported substance over the equivalent weight of the weighed substance. In volumetric analysis, M is the volume of standard solution, and f is the product of the normality of the standard solution times the milligram equivalent weight (in grams) of the reported substance (if M is measured in milliliters). For C and c , the calibrated capacities of the volumetric apparatus should be substituted; if the aliquot part is weighed instead of measured (?), the ratio of the weights is used.

The transmission of the errors of the quantities f, M, S, C , and c into the final result may be easily calculated with the use of the equations given in Table IV. ρ, α, β , and γ represent the absolute errors, and ρ', α', β' , and γ' the relative errors of the quantities R, A, B , and C . The constant errors possess a definite sign, and therefore when substituting, their sign must be considered.

TABLE IV. PROPAGATION OF ERRORS

		R Calculated as:	
		Sum or difference, $R = A + B - C$	Product or quotients, $R = \frac{AB}{C}$
Constant errors	$\rho = \alpha + \beta - \gamma$	(2)	$\rho' = \alpha' + \beta' - \gamma'$
Accidental errors	$\rho = \pm \sqrt{\alpha^2 + \beta^2 + \gamma^2}$	(4)	$\rho' = \pm \sqrt{\alpha'^2 + \beta'^2 + \gamma'^2}$

The formulas are easy to memorize, considering the identical mathematical form of the equations of the same horizontal row and the fact that the left column uses the absolute errors while the right column employs the relative errors. Furthermore, the constant errors are added algebraically, while the accidental errors are added according to Pythagoras.

The usefulness of the tabulated equations may be demonstrated with the use of a few examples. Formulas 2 and 3 indicate that, with the type of functions considered, the constant error of the result is equal to the algebraic sum of the constant errors of the determined quantities. Constant errors may compensate one another. If, however, one of the constant errors is outstandingly large, its effect will be essential to determine the deviation of the result. This fact permits the simple evaluation of the significance of accidents in the performance of an analysis. For example, if one drop (0.05 ml.) of a solution is spilled, or is used for a side test, the relative error is 1000 $\frac{-0.05}{\text{volume of solution in ml.}}$ %; this is

also the relative error caused in any determination hereafter carried out in this solution (Equation 3).

Equations 4 and 5 for the propagation of accidental errors show that the precision of the quantity affected with the greatest uncertainty will essentially determine the precision of the result. Furthermore, the precision of the result is inversely proportional to the square root of the number of measurements and operations contributing identical uncertainties. For example, 100 measurements with average deviations of $\pm 1\%$ combined would furnish a result with the average deviation $\pm 10\%$ (Equation 5). Therefore, it does not seem objectionable to include a large number of measurements or operations in a determination, provided that the precision of the individual procedures is sufficiently high. The practical disadvantage of such determinations lies in the strain imposed on the experimenter, who has to maintain perfection during the performance of a lengthy chain of operations.

The fact that most analytical procedures do not possess a higher precision than $\pm 1\%$ renders the direct determination of the major constituent of a high-grade material impracticable. Even with the use of the hydroxyquinolate as weighing form, the aluminum content of metallic aluminum cannot be found with a higher precision than $\alpha' = \pm 1\%$ or, $99.9 \pm 0.1\%$ Al. Such a result would indicate that the true aluminum content may lie anywhere between 99.5 and 100 per cent. If, however, the sum of the other constituents has been estimated with a precision even as low as $\pm 100\%$, the aluminum content is obtained with satisfactory precision from the difference

$$- \left\{ \begin{array}{l} 100.00 \% \\ 0.10 \pm 0.01 \% \text{ total impurities} \\ \hline 99.90 \pm 0.01 \% \text{ Al} \end{array} \right.$$

In this way the aluminum content is definitely established within the limits 99.86 and 99.94 per cent. Equation 4 thus

confirms the rule that it is unwise to calculate a small quantity (the sum of the impurities in the above case) as the difference of two large quantities.

The use of Equations 1 and 5 will be found helpful in the establishment of a proper correlation of the precisions required in sampling (1), measuring the sample, and aliquot partition, and in the determination of *M*, the measure of the constituent determined. Since all the shortcomings of the chemical procedure usually combine in affecting *M*, this measured quantity often exhibits the lowest precision. In order not to lessen the precision further, it is then advisable to strive for four to five times better precision in all the other operations. A careful planning of the required precision at the different stages of work saves time, labor, and apparatus, especially in routine analyses with large samples where the balances and volumetric apparatus are usually capable of a far higher precision than is required.

In microanalysis the precision of the measuring apparatus is more likely to be below the required level, and in some cases the precision of the results can be directly traced to the limitations of balances, pipets, or burets. Among others, this seems to be true for a series of copper determinations with the use of cupric oxide as weighing form (2).

Summary

Suggestions are made for the establishment of precision and accuracy of chemical methods. An efficient and brief form for reporting the results of the calibration of chemical methods is proposed. The difference of the effect of additive and proportional constant errors is demonstrated. The trans-

mission of errors to the final result is discussed with reference to the use of a general equation for the calculation of chemical analyses. In general it has been attempted to present the statistical aspects of chemical measurements in a form which seems practical for the discussion of analytical data.

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The Sampling and Analysis of Eggs

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THE rapid growth of the egg-breaking industry has led to increased need for accurate and reliable laboratory methods of analysis and control, especially since we are dealing with a product which is highly perishable and cannot be pasteurized as are milk, cheese, and similar dairy products. Preservation is entirely by means of rapid or sharp freezing and any changes in composition of the product packed must be made within a few hours, or before the batch in question is frozen solid.

Last year approximately 180,000,000 pounds of eggs were packed in cans for human consumption. The nature of the pack depends upon the industry for which it is intended. Thus we have egg whites for the baking and candy industries; plain yolk and salted yolk for the mayonnaise and noodle industries; whole eggs, sugar yolk, and glycerol yolk for the baking, ice cream, and confectionery trades; and a number of types of egg products packed to definite specifications as to color and composition.

There has been an increasing need for rapid and reproducible methods of analysis because of the conditions indicated above. Bacteriological tests are equally important, but will be discussed in a subsequent paper.

Sampling

The first difficulty encountered by the chemist in attempting to do control work is the nature of the egg itself. It is very difficult, even in a well-churned batch, to achieve absolute uniformity and the authors have found that samples taken from the top and bottom of the churn vary in total solids content as much as 1 or 2 per cent.

As the result of these discrepancies they determined to take at least three samples from each churnful sampled: one near the top of the churn, the next at about the middle, and the third from the last of the egg in the churn. These three samples were then thoroughly mixed in a quart container, such as a mason jar or milk bottle, and constituted one composite sample which represented with a reasonable degree of accuracy the contents of the churn. The use of a sampling thief, such as is used in the dairy industry, has been suggested, but the authors have not found its use to be practical because of the difficulty in sterilizing it properly at the egg-breaking plant.

Table I indicates the differences in total solids obtained from a single sample and from a composite sample.

TABLE I. TOTAL SOLIDS

	Single Sample %	Composite Sample %	Error %
Whole egg	25.6	26.2	2.3
Whole egg	25.1	26.8	6.3
Salt yolk	48.3	49.0	1.4

All analyses for total solids were performed by the Association of Official Agricultural Chemists' official method for eggs. (An atmospheric oven at 110° to 120° C. yields results as much as 0.5 per cent higher, depending upon the fat content of the egg. This increase in apparent total solid value is no doubt due to the oxidation of the fat and protein present.) The method recommended by the association is used for the sampling of the frozen product.

More recent work has been done on refractometric methods for total solids, and one such has been reported by Bailey (2). The method as reported, however, is not as yet completely satisfactory for accurate control work.

Determination of Glycerol in Egg Yolks

Glycerol yolks are packed chiefly for the baking trade. They contain from 5 to 7 per cent of glycerol and have the property of keeping the cakes baked from them fresh and moist for a longer period of time. Here no A. O. A. C. method applies, but the authors have adapted the following from the association's method for glycerol in meat:

Weigh out from 8 to 10 grams of the egg sample into a 50-cc. beaker, add 1 cc. of 5 per cent acetic acid, and heat over a low flame on a wire gauze with constant stirring until the egg is thoroughly coagulated. The material must not be allowed to char. The lumps of egg should be dry in character and not of a sticky or pasty consistency.

Transfer the coagulated material to a 250-cc. volumetric flask, washing beaker with 25 to 50 cc. of water. Add about 100 cc. of washed alumina cream and make up the mixture to the mark with distilled water. Shake thoroughly, allow to stand for 5 minutes, shake again, and filter through a coarse filter paper. The filtrate should be perfectly clear.

Transfer 25 cc. of the filtrate to a 250-cc. volumetric flask and add 25 cc. of concentrated sulfuric acid and 2 cc. of 10 per cent silver nitrate solution. Add 10 cc. of strong dichromate solution slowly from a pipet, place the volumetric flask on a steam bath, and heat for exactly 30 minutes. Cool and dilute to the mark with distilled water.

Place this solution in a buret and titrate into a beaker containing 100 cc. of water, 15 cc. of sulfuric-phosphoric acid mixture, and 10 cc. of ferrous ammonium sulfate solution measured accurately with a pipet. Add 3 drops of diphenylamine solution as an indicator.

As the titration proceeds the color changes from green to blue-gray to a pure violet at the end point.

Before each determination the ferrous ammonium sulfate solution is standardized against dilute dichromate by placing the dilute dichromate in a buret, and titrating into a beaker containing 100 cc. of water, 15 cc. of sulfuric-phosphoric acid mixture, and 10 cc. of the ferrous ammonium sulfate. Three drops of diphenylamine solution are used as an indicator just as in the determination.

TABLE II. AGREEMENT OF RESULTS

Glycerol in Glycerol Yolk Made Up in Laboratory %	Glycerol by Analysis %	Difference between Duplicates	Blanks Run on Plain Yolk
3.98	4.41	0.07	..
	4.48		
4.73	5.27	0.05	..
	5.22		
5.30	5.90	0.06	0.63
	5.96		
6.36	6.89	0.03	0.52
	6.92		
6.72	7.22	0.04	..
	7.26		

The percentage of glycerol is calculated according to the following formula:

$$\text{When 10 cc. of strong dichromate and 10 cc. of ferrous ammonium sulfate are used}$$

$$\% \text{ of glycerol} = \frac{10 \left[10.0 - \left(\frac{12.5 \times \text{cc. of dilute } K_2Cr_2O_6}{\text{cc. of oxidized glycerol solution}} \right) \right]}{\text{sample weight}}$$

As there is some oxidizable material present in ordinary egg yolk, the determination of glycerol in a prepared glycerol yolk by the dichromate method is on an average 0.5 per cent high. This correction factor was checked by running a series of determinations on plain yolks and calculating the per cent of oxidizable material as glycerol. Table II indicates the agreement of results which may be expected by this method.

The blank indicates that the difference, which averages 0.53 per cent higher than the glycerol in the sample, is due to oxidizable material in the plain yolk. Mallinckrodt c. p. glycerol was used in preparing the laboratory samples. The glycerol assayed 94.5 per cent by the specific gravity method as well as by the chemical method used in determining the glycerol in egg yolks. The reagents were prepared as directed by the Association of Official Agricultural Chemists (1).

Sugar Method

Sugar yolk is packed for the baking and candy trade and although the A. O. A. C. method applies, it is very unsatisfactory because of the difficulty of rapidly determining the end point of the titration. The authors have, therefore, followed the suggestion made by Lane and Eynon (3), and use methylene blue as an indicator. The authors have been able to substantiate the claim of Lane and Eynon, that there is no shift in the titration end point. The use of methylene blue as an internal indicator eliminates the possibility of oxidation of the cuprous oxide by the oxygen of the air, decreases the time required to complete a determination, and increases the accuracy of the method as a whole by permitting a more accurate determination of the end point. It would seem that the complete procedure of Lane and Eynon, including their tables, could well be applied in this case.

The authors have found that it is necessary to analyze the sugar yolk within a short time after sampling unless it is frozen; otherwise a rapid decrease in apparent sugar content is noted, even though toluol or some other preservative be added. The procedure, as modified, is as follows:

Wash about 25 grams of sample into a 200-cc. volumetric flask with 75 cc. of water. Make slightly acid by adding 2 cc. of 5 per cent acetic acid for white or whole egg and 1 cc. for yolk. Mix, and immerse the flask in boiling water until the egg material is thoroughly coagulated. This requires from 15 minutes to 0.5 hour. Cool to room temperature and make up to the mark with washed alumina cream. Shake the sample vigorously for 1 minute, allow it to stand 5 minutes, and then shake for 1 minute. Filter through a dry folded filter.

INVERSION OF SUCROSE. Pipet 25 cc. of the filtrate into a 100-cc. volumetric flask and add 50 cc. of water. Then add slowly from a pipet, while rotating the flask, 10 cc. of dilute hydrochloric acid (sp. gr. 1.1029 at 20° C.). Heat a water bath to 70° C. and regulate the burner so that the temperature of the bath remains approximately at that point. Place the flask in the water bath, insert a thermometer, and heat with constant agitation until the thermometer indicates 67° C. This preliminary heating period should require from 2.5 to 2.75 minutes. From the moment the thermometer in the flask indicates 67° C. leave the flask in the bath for exactly 5 minutes longer, during which time the temperature should gradually rise to about 69.5° C. (if three or four samples are inserted at once in the same bath the initial temperature of the bath should be about 75° C.). Plunge the flask at once into water at about 20° C. When the contents have cooled to about 30° C. remove the thermometer from the flask and neutralize the solution with dilute sodium hydroxide. (The sodium hydroxide solution should be of such strength that 10 cc. of it are equivalent to 10 cc. of the dilute hydrochloric acid used in the inversion.) Fill almost to the mark. Leave the flask in the bath at 20° C. for at least 30 minutes longer and finally make up exactly to volume.

TITRATION WITH STANDARD ALKALINE COPPER SOLUTION. Place 10 cc. of the modified Fehling's solution in a 250-cc. Erlenmeyer flask, and add 10 cc. of water. Heat to boiling and add gradually, from a buret, small portions of the invert sugar solution, until the copper has been completely reduced. The solution must be boiled after each addition to complete the reaction. It is necessary to boil 2 minutes for complete reduction when a larger quantity of the sugar solution has been added in one portion. When the end point is nearly reached and the quantity of the sugar solution to be added can no longer be judged by the color of the solution, add 3 to 5 drops of a 1 per cent water solution of methylene blue and continue the titration until the blue solution is colorless. The sugar solution should be of such strength as to give a buret reading of 15 to 20 cc., and the number of successive additions should be as small as possible.

STANDARDIZATION OF COPPER SOLUTION. Since the factor of calculation varies with the minute details of manipulation, every operator must determine a factor for himself, using a known solution of the pure sugar that he desires to determine and keeping the conditions the same as those used for the determination.

Standardize the solution for invert sugar as follows: Dissolve 4.75 grams of pure sucrose in 75 cc. of water, add 10 cc. of dilute hydrochloric acid (sp. gr. 1.1029 at 20° C.), and invert as directed in the analytical procedure. After inversion neutralize the acid with sodium hydroxide solution and dilute to 1 liter. Ten cubic centimeters of this solution contain 0.050 gram of invert sugar, which should reduce 10 cc. of the modified Fehling's reagent. The strength of the copper solution should never be taken as a constant, but should be checked against the standard sugar solution.

REAGENTS: Soxhlet's modification of Fehling's solution. Mix immediately before use equal volumes of copper sulfate solution and alkaline tartrate solution.

Copper sulfate solution. Dissolve 34.639 grams of CuSO₄·5H₂O in water, dilute to 500 cc., and filter through prepared asbestos.

Alkaline tartrate solution. Dissolve 173 grams of Rochelle salts and 50 grams of sodium hydroxide in water. Dilute to 500 cc. Allow to stand for 2 days and filter through prepared asbestos.

Dilute hydrochloric acid (sp. gr. 1.1029 at 20°/4° C.) contains 20.195 per cent of hydrochloric acid.

Dilute sodium hydroxide. Dissolve 233.0 grams of sodium hydroxide in water and make up to 1 liter. Approximately 10 cc. of this solution will neutralize 10 cc. of the hydrochloric acid solution.

Methylene blue indicator, 1 per cent water solution.

Salt Method

Salt yolks are extensively packed for the mayonnaise trade, since the presence of about 10 per cent of salt not only acts as a preservative but permits the egg to be thawed as a sirupy liquid, whereas a plain yolk when thawed has a gummy, semi-solid consistency. Since salt at 2 cents a pound is very much cheaper than egg yolks at 25 cents a pound, both the packer and

the consumer are vigilant in seeing that the amount of salt added stays very close to the predetermined figure. Consequently, it is necessary to waste as little time as possible in determining the amount of salt present in any given amount of eggs so that any material that is not up to specifications may be promptly reprocessed. There is as yet no A. O. A. C. method for this work. The writers have investigated several methods and have found the procedure developed by B. Harris of the Emulsol Corporation to be the most satisfactory. The analysis of salt yolks, prepared accurately in the laboratory, by this method gave results which checked within 0.1 per cent. Mr. Harris has kindly permitted the authors to submit his method, which is as follows:

Weigh 5 grams of sample into a 500-cc. volumetric flask containing 200 cc. of water. Make up to mark and shake thoroughly. Pipet 50 cc. of this solution into an Erlenmeyer flask, and add 10 cc. of 0.1 N silver nitrate solution with shaking. Add 10 cc. strong nitric acid and 5 cc. of a saturated solution of ferric ammonium sulfate, and titrate with 0.1 N ammonium thiocyanate solution to a permanent light brown color. One cubic centimeter of 0.1 N silver nitrate equals 0.005846 gram of sodium chloride. Correction factor: Subtract 0.3 per cent of sodium chloride from the result.

Acknowledgment

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Determination of Vapors of Chlorinated Hydrocarbons in Air

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IN CONNECTION with certain physiological investigations it was necessary to determine vapor concentrations of a number of chlorinated hydrocarbons in air. Although Barrett (1) has recently described a simple method for esti-

weighing bottle was immersed in warm water to hasten evaporation, but otherwise no change was made from the method already described (2). The results are summarized in Table I.

TABLE I. EFFICIENCY OF THERMAL DECOMPOSITION METHOD WITH VARIOUS CHLORINATED HYDROCARBONS

Compound	Calculated Cl	Trials Made	Range of Concentrations		Known Amounts Found	
			Mg./l. of air	P. p. m.	Range %	Average %
Chloroform	89.10	14	0.073-73.6	15-15,100	97.4- 98.9	98.6
Carbon tetrachloride ^a	93.38	14	0.063-47.8	10- 7,600	97.3-100.6	98.7
s-Dichloroethylene	73.16	14	0.051-89.5	13-22,580	97.7- 99.6	98.5
Trichloroethylene	80.96	14	0.066-90.7	12-16,900	98.0- 99.5	98.7
Tetrachloroethylene	85.52	14	0.073-86.2	11-12,700	98.2- 99.6	98.8
1,1,1-Trichloroethane	79.73	16	0.066-80.1	12-14,680	98.0-100.2	99.0
s-Tetrachloroethane	84.49	14	0.062-87.3	9-12,700	97.9- 98.9	98.3
Propylene chloride	62.77	14	0.069-80.7	15-17,500	98.2-100.0	98.9
Chlorobenzene	31.52	14	0.054-85.0	12-18,500	97.5- 99.2	98.0

^a Data from Olsen et al. (2).

inating trichloroethylene vapors, it was judged best to continue with the thermal decomposition method (2), because of the apparent general applicability of this method to all such vapors.

Accordingly, checks of the thermal decomposition method were made, using eight additional chlorinated hydrocarbons. The samples were fractionally distilled, and boiling points, specific gravities, and refractive indices were checked to assure purity. For the higher concentrations of some materials, the

The method without further modification is suitable for determining the vapor concentrations of a number of chlorinated hydrocarbons over a wide range of concentrations.

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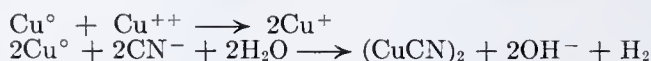
Determination of Metallic Copper in Cuprous Oxide-Cupric Oxide Mixtures

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Cuprous oxide is soluble in cold aqueous ammonia, whereas cupric oxide is but slightly soluble and metallic copper insoluble. The addition of hydrazine sulfate to the reagent tends to reduce any divalent copper entering solution and prevents interaction of cupric copper and metal. If the extraction be carried out in carbon dioxide atmosphere, the metallic copper-cupric oxide mixture may be isolated and the metal determined by direct solution in acid ferric chloride, followed by titration with potassium dichromate.

THE assay of commercial cuprous oxide, according to present approved and accepted methods, involves the direct solution of a weighed sample in acid ferric chloride. The ferrous iron produced during the oxidation of the monovalent copper is determined by titration with a standardized solution of potassium permanganate (1, 7). Inasmuch as metallic copper is also soluble in the reagent, this, if present, is calculated to cuprous oxide in the analysis. It is thus theoretically possible for an equimolar mixture of cupric oxide and metallic copper to be reported as pure cuprous oxide. The influence of copper on the determination has been previously noted (2).

Le Blanc and Sachse (5) analyzed mixtures of cupric and cuprous oxide by allowing the samples to react with hydrochloric acid solutions of potassium iodide. The iodine liberated as the result of the oxidation of the iodide by the cupric salt was determined in the usual manner. When the method was applied to oxide-metal mixtures of the type under consideration, it was found that the copper was oxidized by the liberated iodine at such a speed as to render unreliable an analytical method utilizing this reaction. The direct extraction of both oxides by means of a sodium cyanide solution was advocated by Bonner and Kaura (3). When applied to oxide mixtures containing copper in as fine a state of division as found in commercial samples, serious copper losses have been encountered. Solution of the metal probably takes place according to both of the following equations:



It has been observed that copper losses vary directly with the amount of cupric oxide in the sample and the volume of reagent employed.

The silver sulfate-sulfuric acid method (6) involves a preliminary extraction of metallic copper by boiling the sample with a saturated silver sulfate solution. The residue, consisting of the two oxides mixed with metallic silver, is thoroughly washed and the dissolved copper determined in an aliquot of the filtrate. The method leads to erroneous results because during the extraction finely divided cuprous oxide in contact with the hot sulfate containing solution undergoes disproportionation. The metallic copper produced reacts with excess silver sulfate and is thus dissolved. Apparent copper recoveries are invariably high, the magnitude of the error de-

pending upon the volume of reagent used and the time required to make the extraction.

Cuprous and cupric oxides are soluble in a number of reagents which are without appreciable solvent action upon copper. However, when oxide mixtures containing finely divided metallic copper are dissolved in the salt solutions, a secondary reaction between the cupric or complex cupric ions and copper takes place. The metal is oxidized to a soluble monovalent form with the simultaneous reduction of an equivalent amount of divalent copper. Whereas this reaction may be so slow as to be of little consequence at ordinary temperature, it is of significance at the elevated temperatures required to dissolve all the cupric oxide contained in some of the refractory commercial samples.

In an effort to decrease the solubility of metallic copper in solutions of the type suitable for extraction of oxide mixtures, an attempt was made to find a reducing agent which, when added to the salt solution, would reduce divalent copper to the cuprous state but not to metallic copper, and which would have no solvent action upon the copper itself. Various combinations of ammonium chloride, ammonium carbonate, and magnesium chloride with hydrazine sulfate, hydroxylamine hydrochloride, sodium arsenite, and other reducing agents were investigated. It was found that in an atmosphere of carbon dioxide, a hot 20 per cent solution of ammonium chloride containing 5 per cent of hydroxylamine hydrochloride would dissolve cuprous and cupric oxide with but slight action upon coarse metallic copper. However, when the copper was introduced in the form of a 325-mesh powder, the action was marked and losses of as high as 10 mg. of copper per 100 mg. of dissolved cupric oxide were not uncommon. Solutions containing hydrochloric acid behaved in a similar manner. Ammoniacal ammonium chloride solutions containing either hydrazine sulfate or hydroxylamine hydrochloride could not be used because when hot they react with both cuprous and cupric copper to produce metal. It was found that the cuprous oxide could be quantitatively extracted from oxide-metal mixtures with cold ammonium hydroxide containing ammonium carbonate. Only a very small amount of cupric oxide passed into solution and, in the absence of air, the copper was practically insoluble. The addition of a small amount of hydrazine sulfate was found to be effective in further reducing dissolution of the metal. If the extraction was carried out in an atmosphere of carbon dioxide, the gas served to prevent air oxidation and, as a result of partial interaction with the ammonia, to accelerate solution of cuprous oxide.

Preparation of Solutions

EXTRACTION SOLUTION. Six grams of c. p. hydrazine sulfate were added to 1 liter of aqueous ammonia (sp. gr. 0.90).

FERRIC CHLORIDE. One hundred and fifty grams of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 300 ml. of hydrochloric acid (sp. gr. 1.2) were dissolved in 800 ml. of air-free carbon dioxide-saturated water.

INDICATOR. Two grams of barium diphenylamine sulfonate, 50 ml. of carbon dioxide-saturated distilled water, and 5 grams of sodium sulfate were shaken until a uniform suspension of barium sulfate was obtained. The solution was diluted with 50 ml. of water and allowed to settle. When clear, the supernatant liquor was decanted through a filter and preserved in a dark bottle. The barium diphenylamine sulfonate was obtained from Eastman Kodak Company.

PHOSPHORIC ACID. Ortho, 85 per cent reagent, A. C. S. specifications.

POTASSIUM DICHROMATE. 0.1 *N* solution prepared by dissolving 4.903 grams of reagent quality potassium dichromate in water and diluting to 1 liter.

WATER. Distilled water was boiled vigorously for several minutes and allowed to cool in an atmosphere of carbon dioxide. A slow current of the gas was passed continuously through the storage bottle.

Apparatus

With the possible exception of the filter tube, no unusual apparatus is required for the determination.

The filter is similar to that used by Geilmann and Weibke (4), and consists essentially of a 55-mm. filter tube of the type used for small Gooch crucibles. In the opening is placed a perforated porcelain button which is seated at right angles to the stem. An asbestos pad is built up over the button and securely set by tamping with a glass rod. The filter must be packed in such a manner that the tube may be held in an inverted position without dislodging either the disk or the pad. It has been found that a tube about 60 × 25 mm., with a stem of 110 mm., is a convenient size. A 20-mm. Gooch crucible button serves to support the asbestos pad.

Procedure

A sample of suitable size is weighed out on a small watch-glass, and the glass and contents are placed in a dry, wide-mouthed 250-ml. Erlenmeyer flask. If the material is an electro-lytic product low in copper, it is advisable to take a 1- to 2-gram sample. If it is from a "thermal process," the percentage of copper is usually large and a smaller sample will suffice. The air in the flask is displaced with carbon dioxide (15 to 20 cubic feet per hour) and 10 ml. of ethyl alcohol are added to dissolve any oil present in the sample. Without interrupting the flow of gas, 50 ml. of extraction solution are added. Any lumps of oxide are broken up with a stirring rod. Violent agitation should be avoided. The carbon dioxide inlet should be about 5 cm. (2 inches) above the surface of the liquid. The time required for complete solution of all cuprous oxide varies between 1 and 5 minutes, depending upon the amount and character of the sample under investigation.

When the cuprous oxide has completely dissolved, as evidenced by the total disappearance of red particles, the filter is connected by a suction and slowly lowered into the flask. As soon as the bulk of the solution is removed, the flask is rinsed with carbon dioxide-saturated water and the filtration and washing are continued. Five or six 100-ml. portions of wash water will suffice to remove all the original extraction solution containing the dissolved cuprous oxide. The filter is then disconnected and the flask and contents are pushed back into the flask with a glass rod. Fifteen milliliters of ferric chloride solution are added and the flask is warmed to dissolve the cupric oxide-copper residue. When all particles have disappeared, the solution is cooled to below 40° C. and 10 ml. of phosphoric acid and 3 drops of indicator are added. Dichromate solution is run into the flask until the end point, a change from pea green to intense purple, is reached.

The result is calculated according to the following equation:

$$\frac{N_{\text{K}_2\text{Cr}_2\text{O}_7} \times \text{ml.} \times 0.03179}{\text{wt. of sample}} \times 100 = \% \text{ Cu}$$

The percentage of cuprous oxide in the sample may be determined by dissolving a 0.2-gram sample in ferric chloride and titrating the ferrous iron produced with potassium dichromate in the manner described. It is essential that solution of the sample be carried out in an atmosphere of carbon dioxide or other inert gas. From the volume of dichromate solution equivalent to both the cuprous oxide and copper, the true percentage of cuprous oxide in the sample may be calculated according to the following equation:

$$\frac{\text{ml}_{\text{K}_2\text{Cr}_2\text{O}_7} - \left(\frac{\% \text{ Cu} \times \text{wt. of sample}}{3.179 \times N} \right) \times 0.07157 \times N}{\text{wt. of sample}} \times 100 = \% \text{ Cu}_2\text{O}$$

The calculation of the result is simplified if the sample taken for the copper determination be a simple multiple of that used for the oxide analysis. In actual practice it has been found that a 1.000-gram sample for metallic copper and a 0.2000-

gram sample for cuprous oxide are of convenient size. In this case, one-fifth of the volume of dichromate used in the determination of metallic copper is subtracted from the total titration of the smaller sample to give the volume of dichromate actually equivalent to the cuprous oxide in the sample.

Results of Analysis

The method as outlined above was checked on a variety of cupric oxide, cuprous oxide, and copper combinations under varying conditions. In Table I are to be found the results of one complete series of determinations upon such mixtures.

TABLE I. RESULTS OF DETERMINATIONS

No.	Cu Gram	Weight Taken CuO Gram	Cu ₂ O Gram	Copper Found Gram	Error Gram	Remarks
1	1.000	0.0024	0.24% Cu
2	2.000	0.0045	0.22% Cu
						Extrac- Vol- tion ume Min. Ml.
3	0.0297	0.0291	-0.0006	1 ...
4	0.0582	0.0581	-0.0001	3 ...
5	0.1079	0.1070	-0.0009	5 ...
6	0.0962	0.030	0.0956	-0.0006	1 ...
7	0.0985	0.060	0.0986	+0.0001	3 ...
8	0.1041	0.100	0.1032	-0.0009	5 ...
9	0.0994	0.300	0.0984	-0.0010	3 ...
10	0.1022	0.750	0.1011	-0.0011	3 ...
11	0.1000	...	0.4000	0.0997	-0.0003	1 ...
12	0.1024	...	0.2000	0.1020	-0.0004	3 ...
13	0.1013	...	0.1000	0.1006	-0.0007	5 ...
14	0.1001	...	0.0990	0.0999	-0.0002	3 ...
15	0.1010	...	0.2000	0.1007	-0.0003	3 ...
16	0.1009	...	0.1500	0.1000	-0.0009	3 ...
17	0.1045	0.050	0.1000	0.1048	+0.0003	3 100
18	0.0969	0.050	0.1000	0.0966	-0.0003	3 150
19	0.1064	0.250	0.4000	0.1068	+0.0004	3 200
20	0.1029	0.050	0.9000	0.1030	+0.0001	3 300
21	0.1017	0.150	0.3000	0.1022	+0.0005	3 100
22	0.1023	0.1023	+0.0000	3 100
23	0.1004	0.1005	+0.0001	3 100
24	0.0995	0.151	0.0992	-0.0003	3 100
25	0.1035	0.150	0.1033	-0.0002	3 100
26	0.1023	...	0.4000	0.1015	-0.0008	3 100
27	0.1009	...	0.3500	0.1000	-0.0009	3 100
28	0.1078	0.050	0.7000	0.1079	+0.0001	3 100
29	0.1001	0.050	0.0200	0.0992	-0.0009	3 100
30	0.0993	0.1000	0.6000	0.0988	-0.0005	3 100
31	0.1049	0.050	0.3000	0.1040	-0.0009	3 100
32	0.1034	0.100	0.0600	0.1032	-0.0002	3 100
33	0.1010	0.400	0.1000	0.1000	-0.0010	3 100

TABLE II. ANALYSIS OF COMMERCIAL SAMPLES OF CUPROUS OXIDE

Sample No.	"Cu ₂ O" Direct %	Cu Found %	Cu ₂ O Present %
1a	98.68	10.38	75.16
		10.44	75.15
2m	104.20	11.84	77.43
		11.84	77.42
3m	88.84	1.27	85.98
		1.29	85.90
4m	99.48	9.54	77.97
		9.54	78.05
5L	95.61	0.26	95.00
		0.24	95.01
6T	6.92	0.22	6.49
		0.22	6.46

The cuprous oxide used was a commercial grade electrolytic product. The cupric oxide was a 325-mesh screen fraction from reagent quality material. The metallic copper was 325-mesh electrolytic copper powder which had been previously extracted with the ammonium hydroxide-hydrazine sulfate solution, washed with water, alcohol, and ether, and dried in a vacuum desiccator. Results are corrected for copper contained in the cuprous oxide used in the experiments.

The errors are of about the same magnitude, irrespective of the amounts of material taken or the volume of extraction solution used. It was found that, if the ammonium hydroxide-hydrazine sulfate solution was allowed to stand in contact with the samples for more than 10 minutes, the

loss in copper sometimes amounted to more than 2 mg. In one experiment, the reagent was allowed to act upon a mixture of 0.4 gram of cupric oxide, 0.3 gram of cuprous oxide, and 0.1 gram of copper for 1 hour. At the end of this time, 0.0050 mg. of copper had dissolved. Care must be taken not to allow the extraction solution to become saturated with carbon dioxide. If the gas inlet to the flask be placed beneath the surface of the liquid, solubility errors will be increased.

Fifteen determinations of metallic copper made upon a sample of electrolytic cuprous oxide indicated an average value of 0.25 per cent, with a maximum deviation of 0.01 per cent and an average deviation of ± 0.006 per cent. The same number of determinations on a sample of "thermal process" cuprous oxide yielded an average value of 1.07 per

cent, with a maximum deviation of 0.02 per cent and an average deviation of ± 0.008 per cent.

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Quantitative Determination of Cadmium and Lead in Zinc

Using a Grating Spectrograph with a Sector Disk

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THIS work was an attempt to determine the possibility of using a replica grating spectrograph for making a quantitative determination of metallic impurities in compounds. The specific problem at hand was the quantitative determination of cadmium and lead impurities in zinc. It was desired to take a specimen of unknown content and, by a simple procedure requiring approximately 15 minutes, excite the spectrum of the specimen, obtain a spectrogram, and from this spectrogram obtain the quantity of the impurities present. A method suitable for commercial use was desired.

The grating is mounted in the Rowland fashion, with the camera fixed to photograph the first order of the visible range. It is possible, by rotating the grating about its vertical axis, to obtain wave lengths from 10,000 Å. to 2100 Å., the ultraviolet just outside the visible range being the most useful.

The logarithmic sector disk is placed as near the slit as possible, and the mounting made stigmatic by placing the arc at the focal center of a convex lens, thus rendering a parallel beam of light on the slit. The sector disk is caused to rotate at a speed of 300 r. p. m. and is adjusted so that approximately 3-mm. length of the 16-mm. slit is left open at all times. The remainder of the slit opening is varied during the time of exposure as the sector disk rotates in front of it. The variation of time along the slit causes the lengths of the lines on the film to vary according to the intensity of the line.

A typical spectrogram is shown in Figure 1. Assuming the percentage content of the element present to be directly proportional to the intensity of its characteristic lines for small percentages and the blackening of the film to vary logarithmically with the intensity falling upon the film, then the lengths of the lines produced by different percentages of the element plotted against the percentage of the element should result in a curve which is a straight line. The curves were actually found to vary slightly from straight lines, as seen in Figure 2.

The arc consists of two vertical graphite electrodes, which must be of the purest graphite and approximately 0.6 cm. (0.25 inch) in diameter. The lower (positive) electrode is drilled with a 0.39-cm. (0.156-inch) drill to a depth of 0.6 cm. (0.25 inch) and the sample under investigation is stuffed into this basin. The method of excitation of the spectra of slowly volatilizing substances is very effective because of the high temperature reached by the carbon arc. The current through the arc was about 5 amperes and the voltage supply 220 volts direct current. The voltage drop across the arc was 40 volts and the arc gap 1 cm.

It is essential in this type of work that the current and voltage drop across the arc, and consequently the energy consumed by the arc, remain constant. An inductance may be placed in series with the arc and resistor to stabilize the arc current. Any other proved method of excitation of the spectra of the elements should prove as satisfactory as the one used here.

Because sulfates are stable in the arc, the sulfate form of the sample was used for these tests. Any metal sample may be converted into the sulfate form by first dissolving the sample in concentrated nitric acid, then adding concentrated sulfuric acid and evaporating the solution to dryness under a hood. After the residue has completely dried it is ground in a mortar and



FIGURE 1. SPECTROGRAM

mixed thoroughly. In this work, samples were prepared from chemically pure zinc sulfate, lead sulfate, and cadmium sulfate. These were thoroughly dried, weighed out in known amounts to obtain the desired percentages, then ground and mixed in an agate mortar. Percentages are expressed in terms of weight per cent of zinc, lead, and cadmium metal present rather than in terms of total weights of salts present.

Several technics of preparing the sample for its spectra excitation have been reported (1, 2, 3). In this experiment the one chosen was that of placing the same amount of powdered specimen in the lower electrode basin and burning the arc for a definite period. This time of exposure was 1 minute. The films were developed for 1 minute at about 25° C. The lines were measured with a small millimeter scale and magnifying glass in diffused white light. Measurements of lengths of the spectral lines can be repeated to within 0.2 mm.

TABLE I. CADMIUM IMPURITY IN ZINC

Cadmium %	Length of Line (3261 Å.) Mm.
0.001	5.1
0.002	5.5
0.003	5.8
0.007	6.8
0.012	8.0
0.020	9.8

TABLE II. LEAD IMPURITY IN ZINC

Lead %	Length of Line (2663 Å.) Mm.	Length of Line (2833 Å.) Mm.
0.001	...	4.4
0.002	...	5.0
0.003	1.8	5.3
0.008	2.8	6.8
0.012	3.6	7.8
0.020	4.9	9.0

Table I shows the tabulated results for cadmium, and Table II, for lead. These results are shown graphically in

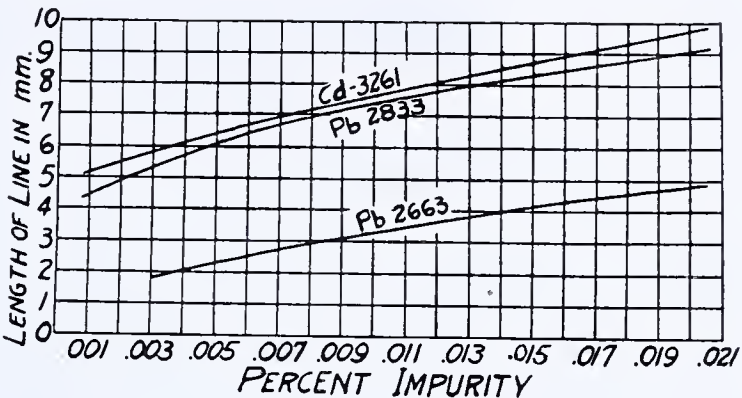


FIGURE 2. CADMIUM AND LEAD IMPURITIES IN ZINC

Figure 2. The 2663 Å. line of lead fails to appear below 0.003 per cent lead.

It can be concluded from these results that cadmium and lead impurities in zinc can be easily detected down to 10 parts in one million, with an accuracy of 10 to 15 per cent. The lengths of the cadmium and lead lines at 0.001 per cent indicate that percentages of these impurities below 0.001 per cent could be detected and the amounts estimated.

Acknowledgment

It is a pleasure to acknowledge the loan of the replica grating spectrograph and accessory apparatus by the Central Scientific Company of Chicago, without which this investigation could not have been carried on.

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Determination of Manganese in 18-8 Corrosion-Resisting Steel

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STEELS of the 18-8 (chrome-nickel) type dissolve rather slowly in sulfuric acid, but rapidly in aqua regia. Both the nitric and hydrochloric acids are easily removed by perchloric acid at its boiling point. After cooling and diluting, the chromium is precipitated during the neutralization with zinc oxide emulsion. After correctly preparing the solution and titrating the manganese, the results on standard samples ran about 0.1 per cent too low. It was possible that a portion of the manganese had separated as a chromate, or that some manganese was oxidized to the trivalent form by the perchloric acid and came out as the hydroxide upon the addition of the zinc oxide emulsion.

To take care of either possibility, sulfurous acid was added to the solution which had been fumed with perchloric acid and diluted. Completion of the routine analysis showed exact checks with the sulfuric acid solution method.

Weigh 1 gram of drillings into a 150-cc. beaker. Add 25 cc. of the dissolving solution (1000 cc. of water, 250 cc. of nitric acid, and 50 cc. of hydrochloric acid), and heat until solution is complete. Add 10 cc. of perchloric acid (technical), and boil until the chromium is oxidized and the perchloric acid starts to condense on the cover and walls of the beaker. Remove from the hot plate. Wash the acid down with water. Dissolve the residue with water, dilute to about 30 cc., and add 10 cc. of a saturated sulfur dioxide solution (10 cc. of a 25 per cent sodium sulfite solution will do) to reduce the chromium. Boil 2 or 3 minutes. Cool.

Neutralize with freshly prepared zinc oxide emulsion, using but a slight excess. Cool, and make up the solution to 250 cc. in a volumetric flask.

Empty into a 400-cc. beaker and stir; the chromium will settle in a short time. Pipet out 50 cc. into a 150-cc. fat-extraction flask. Add 30 cc. of a mixture of 3600 cc. of nitric acid, 810 cc. of sulfuric acid, 300 cc. of orthophosphoric acid, 232 grams of silver nitrate, and 13,860 cc. of water. Heat until the solution is clear. Add 20 cc. of 6 per cent ammonium persulfate solution, and heat carefully till bubbles of oxygen form on the surface of the liquid. Cool. Titrate with arsenite solution of such strength that 1 cc. is equivalent to 0.1 per cent of manganese on the 0.2-gram sample.

Using U. S. Bureau of Standards sample KA2-S, 5.5 cc. were required by both this and the sulfuric acid solution methods.

Discussion

This solution method is faster than solution in sulfuric acid, or directly in perchloric acid. It has the further advantage that iron is not separated from solution by the zinc oxide. Thus the permanganate solution which is brought to the arsenite buret is in almost the same condition as that of a low-chromium steel which was probably used to standardize the original arsenite solution. The accuracy is the same as that of the sulfuric acid solution method.

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Microdetermination of Fluorine

Elimination of Effect of Chloride

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WILLARD and Winter (3) have made the most valuable contribution to fluorine analysis in recent years. They proposed the separation of fluorine from substances which interfere with its determination by distillation of hydrofluosilicic acid and the titration of the evolved fluorine, in an alcoholic solution, with standard thorium nitrate solution. Because the indicator which they employed combined with fluorine, being a lake of zirconium and sodium alizarin sulfonate, and was otherwise inconvenient, this writer (1) simplified the procedure by using an aqueous solution of sodium alizarin sulfonate as the indicator. This modified procedure has become the most generally used fluorine analytical method and has undergone further modification, chiefly at the hands of Hoskins and Ferris (2), who present an adequate review of the literature.

There is need for a simple procedure applicable to the determination of very small quantities of fluorine, since many naturally occurring substances contain little of this element and large samples must be employed. The manipulation of large samples is inconvenient and the quantity of extraneous substances thus introduced causes inaccurate results. The technic herewith presented permits the determination of microgram quantities of fluorine with an accuracy fully as great, if not greater than, that obtained with the macro-procedure or semi-microprocedure previously published.

It was not possible to obtain satisfactory results by direct adaptation of the previously described methods. The adaptation consisted in a reduction in volume of the alcoholic solution for titration to 2 cc. and in the use of 0.0004 *N* instead of 0.01 or 0.001 *N* thorium nitrate solution. The results of titration of 1.25 to 10.0 γ of fluorine in 48 per cent alcohol fell on a straight line when plotted, but the plotted data of the titration of 0.5 to 1.25 γ fell on another line (Figure 1). The smaller amounts of fluorine required more thorium nitrate than that which corresponds to the amounts predicted from the projection of the first-mentioned line. Attempts to correct the lack of equivalence of the thorium nitrate solution for amounts of fluorine greater and less than 1.25 γ by the following methods failed: (1) alteration of the amounts of hydrochloric acid of various dilutions added in excess of that required to adjust the color of the indicator to greenish yellow; (2) use of nitric acid for adjustment of the acidity of the solutions for titration; (3) use of the monochloroacetic acid buffer of Hoskins and Ferris; (4) the addition of 1 drop of 1 *N* sodium chloride to the solution to produce approximately

The fluorine content of biological and some other materials is so low as to require the use of a micromethod for its accurate determination. Based on the titration of fluorine in aqueous solution with thorium nitrate, such a procedure has been developed. The use of aqueous rather than the usually employed alcoholic solution gives better results because the equivalence of the thorium nitrate solution for fluorine through the range 0.5 to 10 micrograms of fluorine is exact, a situation which does not obtain when alcoholic solutions are employed. In aqueous solution the concentration of perchloric acid required to influence the results is greater than in alcoholic solution. The amount of perchloric acid evolved is reduced by distilling hydrofluosilicic acid in the presence of sodium perchlorate. The fluorine content of some samples of dental enamel, dentine, and inorganic phosphates has been determined. A procedure for the removal of chloride, when present in interfering amounts, by the use of silver perchlorate is presented.

equal ionic concentration of all solutions; (5) the use of a thorium nitrate solution in 48 per cent alcohol; (6) various combinations of these procedures.

The results obtained on the distillation and titration, in alcoholic solution, of 10 to 25 γ of fluorine, introduced as sodium fluoride, averaged 20 γ in excess of the theoretical amount even though the aliquots contained 2.5 γ of fluorine and the Hoskins-Ferris buffer was employed. That the cause of the high results was due to some substance collected during the distillation was shown by experiments in which no fluorine was distilled. Twenty-five gamma of fluorine were added directly to the receiver contents and the results of titration were again 20 γ in excess of the theoretical quantity. The interfering agent was found to be perchloric acid collected in the receiver. The titration of dilute solutions of perchloric acid showed that this acid behaved as fluorine in proportion to its concentration. The amount of perchloric

acid volatilized varies with the temperature of distillation and volume of distillate. At 140° the equivalent of about 2 cc. of 0.1 *N* acid is collected in 150 cc. of distillate. At 130° the distillation blank is reduced to the equivalent of 8 γ of fluorine but the recovery of fluorine is only 70 per cent of the theoretical quantity. While the distillation blank may be maintained reasonably constant under controlled conditions its magnitude and variations prevent the accurate determination of small quantities of fluorine.

Other expedients which were tried in attempts to eliminate the effect of perchloric acid but which were unsuccessful were (1) reduction of the perchloric acid with hydrazine hydrate; (2) its removal by aëration of the acidified solution; (3) redistillation of the concentrated receiver contents from phosphoric and sulfuric acids; (4) the use of the Hoskins-Ferris buffer; and (5) the use of a distilling flask provided with a "spray trap."

Principle of Method

It was found that the results of titration of 0.5 to 10 γ of fluorine in 1 cc. of aqueous solution fell on a straight line when plotted (Figure 1) and also that, under this condition the amount of perchloric acid collected in the distillate did not influence the results when the receiver contents were concentrated to a volume no less than 10 cc. The determination of 5 γ or less of fluorine requires that the receiver content be evaporated to at least 5 cc., in which case the increase in concentration of perchloric acid in 1-cc. aliquots causes high

results (Tables I and II). The amount of perchloric acid collected in the distillate can be reduced, it was discovered, as much as 50 per cent by the introduction of sufficient sodium perchlorate in the distilling flask. This salt, since it elevates the boiling point of the solution, reduces the concentration of acid per unit volume in the contents of the distilling flask and thus diminishes the quantity of acid volatilized.

Hoskins and Ferris (2) reported that good results were obtained in the titration of alcoholic solutions only when buffered at pH 3.5. It was found that the use of the buffer is unnecessary if sufficient care is used to adjust, with dilute hydrochloric acid, the acidity of the solutions before titration (figure 1). However, because of the convenience gained by employing the buffer, its use has been adopted. While the pH of the monochloroacetic acid-sodium salt buffer is 3.5 in 48 per cent alcohol, its pH is 2.8 in water. For titration in aqueous solution a 2 M formic acid-sodium salt buffer was prepared and used for a short time. The pH of the undiluted buffer, by determination with the glass electrode, was 3.48 and when diluted 40 times was 3.68. One drop of this buffer was added to each 1-cc. aliquot, after preliminary adjustment of the acidity of the solutions to the transition interval of the indicator, but it was found that there was a tendency for amounts of fluorine below 2 γ to require too much thorium nitrate. By the use of the Hoskins-Ferris buffer, even though the theoretical and determined pH is 2.8 in aqueous solution, exact equivalence of fluorine for thorium nitrate throughout the range 0.5 to 10 γ of fluorine was observed. Thus the optimum pH for the titration of fluorine in 48 per cent alcoholic and in aqueous solutions vary, although the identical buffer is employed.

Special Reagents and Procedure

Prepare a stock solution of sodium fluoride containing 1 mg. of fluorine per cc., and from this solution make others containing 12, 5, and 10 γ of fluorine per cc. The sodium fluoride used in the work described in this report was synthesized in this laboratory and its purity checked by conversion to sodium sulfate. Sodium perchlorate: Neutralize 60 per cent acid with strong sodium hydroxide and evaporate the solution until it boils at 1° C. Collect the crystals which form on chilling the solution and dry them at 110° C. Silver perchlorate: In the dark room add a slight excess of freshly prepared silver oxide to 40.3 grams of 60 per cent acid. Filter and dilute the solution to 250 cc., giving a solution containing 1 gram of the salt per 5 cc. Store the product in a dark bottle. Buffer: Neutralize, with sodium hydroxide, 50 cc. of 4 M monochloroacetic acid to phenolphthalein, add 50 cc. of 4 M monochloroacetic acid, and dilute to 200 cc. Water: Ordinary distilled water apparently contains a trace of fluoride, which is removed by redistillation from alkali. Titration vessels: Cylindrical vials approximately 4.5 \times 1.4 cm. are used. Those in which dentists receive gold foil are ideal and can be obtained in quantity. They should be selected for uniform size.

The apparatus employed in the distillation of hydrofluosilic acid is identical with that used by Willard and Winter (5). If the water employed in the distillation is freshly boiled and transferred to the dropping funnel while warm, the troublesome formation of bubbles in the capillary tube leading from the dropping funnel is prevented and bumping during distillation is reduced.

Charge the 50 cc. distilling flask with the sample, 3 glass beads, 10 gram of acid-washed and ignited quartz, 10 cc. of water, 5 cc. of 60 per cent perchloric acid, and, if the sample contains 5 γ or less of fluorine, 6 grams of sodium perchlorate. Heat the contents of the distilling flask to 140° and collect 150 cc. of distillate. The temperature of distillation and volume of distillate were established by experiment as optimal for quantitative evolution of fluorine and minimal distillation of perchloric acid. Maintain the receiver contents, during their collection, just alkaline to phenolphthalein with dilute sodium hydroxide. Evaporate the receiver contents, while alkaline, to a small volume, cool the solution, and make it just acid to the indicator with hydrochloric

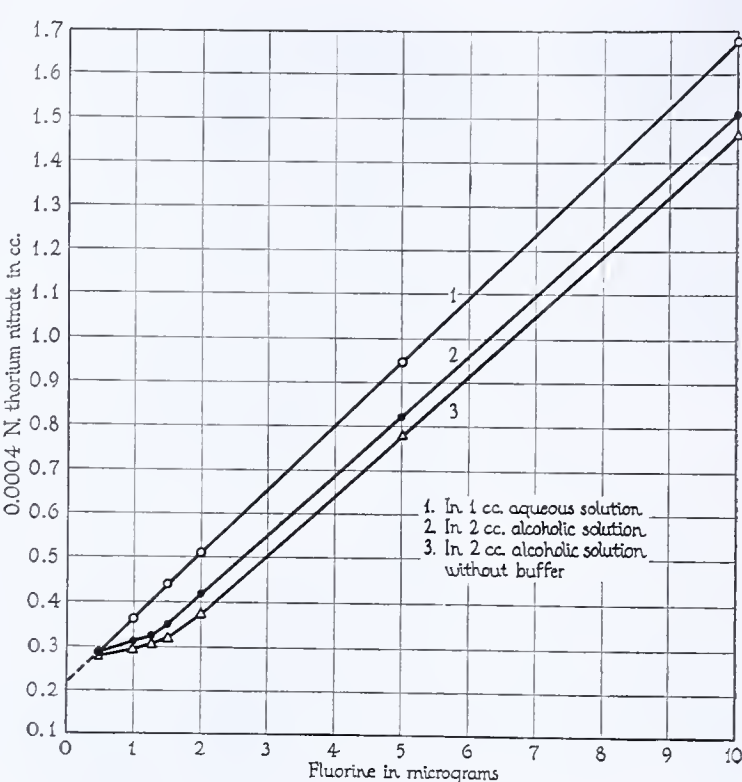


FIGURE 1. TITRATION CURVES OF FLUORINE WITH THORIUM NITRATE

acid. If the sample contains 5 γ or more of fluorine, dilute the solution, in a volumetric flask, to 10 cc. If the sample contains 5 γ or less of fluorine, evaporate the receiver contents to 5 cc. and take the aliquots (1 cc.) for titration by weight. Transfer four 1-cc. aliquots to titration vessels provided with a small glass stirring rod and add to each one drop of 0.05 per cent aqueous solution of sodium alizarin sulfonate. Add split drops of dilute (about 0.03 N) hydrochloric acid until the transition color of the indicator appears (light orange color). Add one drop of the buffer solution and titrate with 0.0004 N thorium nitrate solution (1 cc. equals 7.3 γ of fluorine). Use a buret graduated at each 0.01 cc. and read to the nearest 0.005 cc. Standardize the thorium nitrate solution concurrently by titration, in a similar manner, of 1-cc. volumes of standard fluoride solutions containing 1, 5, and 10 γ of fluorine. The end point of the titrations is recognized by the appearance of the first perceptible pink color of the thorium lake which matches the color of a reference solution. Having once determined the volume of thorium nitrate required to develop a satisfactory color in the titration of 5 γ of fluorine, add this amount to 1 cc. of such a solution and employ the color of resulting solution for reference in the titration of the unknowns and standards. Determine the titration blank by substituting the results of titration of 1 and 10 γ of fluorine in the 2-point equation for a straight line.

y - y1 / x - x1 = y2 - y1 / x2 - x1

and calculate the y-intercept or titration blank (intersection of the ordinate and dotted line, Figure 1). From the results of titration of 1, 5, and 10 γ of fluorine, calculate the mean equivalence of the thorium nitrate solution.

Accuracy of Results

The results obtained on the analysis of sodium fluoride solutions containing 2 to 25 γ of fluorine are shown in Table I. Each result, as do all results presented in this paper, represents a separate distillation and each was calculated from the mean fluorine content of four aliquots.

TABLE I. ANALYSIS OF SODIUM FLUORIDE

Total Fluorine Present	Fluorine Found	Average Fluorine Found	Average Error
γ	γ	γ	%
25	24.8, 24.3, 24.9, 24.4, 24.6	24.60	-1.6
10	9.4, 10.2, 9.8, 10.2, 10.0	9.92	-0.8
5	5.7, ^a 5.4, ^a 5.15, ^a 5.3, ^a 4.85, 5.1, 4.8, 5.1	4.96	-0.8
2	1.90, 2.06, 2.02, 1.86	1.96	-2.0

^a Without NaClO₄. Not included in mean.

TABLE II. DISTILLATION BLANK DETERMINATIONS

Fluorine Added to Receiver	Fluorine Found	Average Fluorine Found	Average Error
γ	γ	γ	%
25	24.1, 24.8, 24.2, 23.9, 25.1, 25.2	24.5	-2.0
10	9.60, 9.75	9.67	-3.3
5	5.5, ^a 5.4, ^a 5.5, ^a 5.2, 4.9	5.05	+1.0
2	2.06, 1.94	2.00	0.0

^a Without NaClO₄. Not included in average.

TABLE III. ANALYSIS OF PHOSPHATES

Phosphate	Fluorine Found		
	Single distillation %	Double distillation %	10 γ fluorine added to residue γ
"Ca ₃ (PO ₄) ₂ "	0.631	0.615	10.3
Ca(H ₂ PO ₄) ₂	0.0131	0.0134	9.5
NaH ₂ PO ₄	0.0000
Concd. H ₃ PO ₄	0.0015

That the accuracy of the above analyses was not due to balancing errors is shown by the results in Table II, in which determinations the fluorine was not distilled but added directly to the receiver contents. In this manner all uncertainty as to the quantitative evolution and collection of fluorine was removed, and if any substance had been collected in the distillate which influenced the analyses the results would have departed markedly from the theoretical values.

The most severe test of the effect of phosphate, which might be expected to interfere by causing high results, is the analysis for fluorine in inorganic phosphates. In Table III are shown the results of analysis of reagent grade materials.

The surprisingly high fluorine content of the calcium phosphates was shown to be real by the results presented under the column "double distillation." The receiver contents were concentrated, while alkaline, and the fluorine was redistilled as hydrofluosilicic acid in the usual manner. If phosphate were collected in the first distillate, the amount collected in the second distillate would have been greatly reduced and the apparent fluorine content of the materials by double distillation would have been correspondingly lower than by single distillation. The data in the last column were obtained on the distillation of and analysis for 10 γ of fluorine added to the residue in the distilling flask after volatilization and collection of the fluorine originally present in the material. If any interfering substance, particularly phosphate, distilled in any event, it would also have been collected when the 10 γ of fluorine were volatilized and the results of analysis of the receiver contents would have been very much higher than the theoretical quantity. The high fluorine content of the calcium phosphates is probably explained by the insoluble nature of the phosphates and of calcium fluoride. The "tricalcium phosphate" is at least partially hydroxy-apatite and the fluorine contained in this material is probably combined as fluo-apatite. Being combined in insoluble states, the fluorine was thus not removed from the calcium phosphates by washing during their preparation.

Further proof of the accuracy of the method is afforded by the results of analysis of unashed enamel (0.7 per cent protein) and dentine (22 per cent protein) of the same teeth, as shown in Tables IV and V. The sample weights varied from 45 to 70 mg.

The results of the multiple distillation determinations one of which (Table IV) was a triple distillation, and the above considerations in regard to the reduction of phosphate by successive distillations again show that phosphate, or any other material which interferes with the accuracy of the procedure, is not collected in the receiver. The recoveries

of 10 γ of fluorine added to the residue in the distilling flask after distillation of the fluorine originally present in the materials are further proof of the accuracy of the results. An indication of the completeness of the recovery of the fluorine contained in the substance is afforded by the determinations in which extra fluorine was added to the original enamel or dentine.

The lower limit of quantity of fluorine for which the method is applicable has not been determined by experiment. Since the aliquots of the 2 γ determinations (Table I) contained 0.4 γ of fluorine, the lower limit seems to be in the vicinity of 0.4 γ . The difficulties attendant on the concentration of the distillate to 1 or 2 cc. have discouraged attempts to determine fluorine in a total amount of a fractional quantity of a microgram.

Elimination of Effect of Sodium Chloride

Any chloride in the sample is distilled as hydrogen chloride and in the preparation of the distillate for analysis is converted to sodium chloride. Hoskins and Ferris reported the permissible upper limit of sodium chloride to be slightly lower than 0.1 M in the titration of 57 γ of fluorine in 50 cc. of alcoholic solution. In the present work the interfering concentration of sodium chloride in the titration of 10 to 0.5 γ of fluorine in aqueous or alcoholic solution was determined to lie between 0.003 to 0.004 gram per 1 cc. Therefore, if the distillate is made to 10 cc., the sample may contain as much as 0.018 gram of chloride. The materials whose fluorine contents are reported above contained much less than the allowable quantity of chloride. However, many substances, especially biological materials, contain large amounts of this element. The accurate fluorine analysis of these materials requires the removal of the chloride from the distillate. The addition of an amount of sodium chloride equal to that contained in the unknown to the reference solution used in the titration does not correct the error in the determination of microgram quantities of fluorine because the recognition of the end point is difficult in the presence of a large excess of sodium chloride. Furthermore, the chloride content of the distillate must be determined if the correct amount of sodium chloride is to be added to the reference solution.

Since silver fluoride is soluble, the possibility of removing chloride from the distillate as the silver salt followed by re-

TABLE IV. ANALYSIS OF SOUND HUMAN DENTAL ENAMEL

	Fluorine Found %	Average Fluorine Found %
Single distillation	0.0163, 0.0154, 0.0164, 0.0160	0.0160
Single distillation with NaClO ₄	0.0157, 0.0162	0.0160
One redistillation	0.0153, 0.0155, 0.0158	0.0155
Two redistillations	0.0163	0.0163
	Micrograms	Micrograms
10 γ F added to residue	10.0, 10.6, 9.8	10.1
5 γ F added to original enamel	4.7, 4.9	4.8

TABLE V. ANALYSIS OF SOUND HUMAN DENTINE

	Fluorine Found %	Average Fluorine Found %
Single distillation	0.0200, 0.0208, 0.0204, 0.0207 ^a	0.0204
One redistillation	0.0206	0.0206
	Micrograms	Micrograms
10 γ F added to residue	9.8	9.8
10 γ F added to original dentine	10.4	10.4

^a With NaClO₄.

distillation of the fluorine in the filtrate was apparent. Silver nitrate cannot be employed as the precipitant, since the nitrate which replaces the chloride is volatilized in the second distillation and introduces as large an error in the titration of fluorine as does chloride. The use of silver oxide is not practical for the removal of large amounts of chloride, since silver chloride is precipitated only on the surface of the particles. Silver perchlorate was found to be the ideal precipitant, since sodium perchlorate is formed in an amount equivalent to the sodium chloride contained in the solution. It was shown above that the presence of sodium perchlorate in the distilling flask is advantageous since it reduces the amount of perchloric acid volatilized. The second distillates, on acidification to phenolphthalein, were found, in many instances, to possess a slight color which caused low results in the titration of the fluorine in the aliquots. No procedure was discovered whereby the production of the color could be prevented, nor has its source been entirely identified. However, the color can be removed with activated charcoal, thus permitting the accurate titration of the solution for fluorine.

If the sample is soluble, dissolve it in 150 cc. of water and precipitate the chloride as described below. Perform the first distillation of solids as described above, omitting phenolphthalein from the receiver contents. Maintain the receiver contents alkaline to phenolphthalein paper with 1 *N* sodium hydroxide. Since the greater part of the hydrogen chloride is evolved when the flask contents have boiled at 140° C. for 5 minutes, use 0.1 *N* sodium hydroxide during the last half of the distillation. Make the distillate acid with dilute perchloric acid and add, with constant stirring, silver perchlorate solution until the silver chloride coagulates. Continue the addition of silver perchlorate in 0.1-cc. increments until a drop of the solution produces a red color on filter paper which has been impregnated with 5 per cent potassium chromate. Make the solution alkaline to phenolphthalein paper and heat it to boiling to promote coagulation of the precipitate. After cooling the solution, filter it through retentive paper. All operations during the precipitation of the silver chloride should be carried out in subdued light.

Evaporate the filtrate to about 10 cc. and filter off any silver oxide which may have formed during the concentration. Evaporate the filtrate to about 5 cc. and transfer it to the distilling

flask together with 4 to 6 grams of sodium perchlorate. Perform the second distillation in the usual manner and maintain the receiver contents alkaline to phenolphthalein. Evaporate the distillate to a small volume, make it acid to the indicator, and dilute the solution to the optimal volume. Add 0.25 gram of activated charcoal per 10 cc. of solution and shake the flask for about 3 minutes. Filter the solution, using dry apparatus, and titrate 1-cc. aliquots of the filtrate in the usual manner.

TABLE VI. DETERMINATION OF 10 MICROGRAMS OF FLUORINE IN PRESENCE OF ONE GRAM SODIUM CHLORIDE

Fluorine Found		Fluorine Found	
Undecolorized	Decolorized	Undecolorized	Decolorized
γ	γ	γ	γ
9.0 ^a	9.7 ^a	9.2 ^{a,b}	...
9.3 ^a	10.1 ^a	8.8	...
8.9	9.8	9.4	...
9.3	10.2	9.0	...
9.0	9.7	9.2	...
..	9.7	9.3	...
..	9.8	9.0	...
9.2 ^{a,b}	10.3		
	..		
Average		9.1	9.9
Av. error, %		9.0	1.0

^a First distillation omitted.

^b Blank. Fluorine added to distillate.

The results shown in Table VI were obtained when the determinations were begun in the presence of 1 gram of sodium chloride. Two determinations of the fluorine content of the pooled human dental enamel mixed with 1 gram of salt showed the enamel to contain 0.0162 and 0.0155 per cent of fluorine. Titration of the undecolorized distillate indicated only 0.0151 and 0.0137 per cent of fluorine. The calculated amount of fluorine in the first sample, on a basis of 0.0160 per cent of fluorine as previously determined, was 8.4 γ and 8.1 γ in the second.

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RECEIVED July 8, 1936.

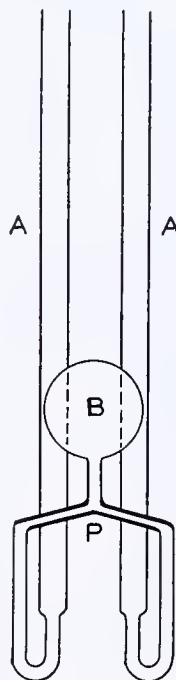
A Sensitive Thermoregulator

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THIS regulator is a modification of the type that depends on the change in vapor pressure of a volatile liquid with change in temperature. It is constructed in such a way that no seals are required for the electrical leads and no contact points are present to corrode, and, finally, is made extremely sensitive by employing the principle of the differential manometer. Since the capacity of the regulator is large and the electrical circuit is broken with a rise in temperature, no relay is needed. It can be used directly on a 110-volt line for currents up to 2 amperes.

The diagram shows the construction of the regulator. The tubes, A and A', are made large (10 mm.) compared with the heavy-walled tube (3 mm.) at P where contact is made. The bulb, B, should not be less than 3 cm. in diameter. The total length of the apparatus is about 20 cm.

For temperatures between 15° and 40° C., the apparatus is completely filled with isopentane, and some inert gas, such as nitrogen, hydrogen, or butane, is introduced through a capillary until half the isopentane in the bulb is displaced. Mercury is poured into the arms until it stands about 10 cm. high. The bulb is gently warmed and pentane is then expelled until the two mercury columns meet at P, when the regulator is cooled to approximately the temperature of operation. Further adjustment may be made by adding or removing small amounts of mercury. It is convenient to use a small plunger fitted through a small stopper in the end of one arm for the fine adjustment.



The current is conducted to the mercury through No. 18 Nichrome wire. A 1-microfarad condenser is connected across these leads to prevent arcking and the formation of colloidal mercury.

The sensitivity of the regulator depends on the angle at which the two mercury columns meet at P. A range of 0.05° C. is sufficient to make and break the contact in the regulator in use in this laboratory.

All regulators of this type are subject to fluctuations in barometric pressure. This could be eliminated by using ground-glass stoppers in tubes A and A', but it would complicate the apparatus and require sealed-in leads. The temperature of the bath being regulated does not usually vary more than $\pm 0.2^\circ$ C. from this cause and can easily be adjusted before beginning an experiment.

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Fat-Extraction Apparatus for Feeds

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THE ordinary Soxhlet extraction apparatus is not only fragile but requires a large amount of space, especially where large batteries are necessary as in feed control work.

Figure 1 shows a compact, rugged, and easily operated unit which has been in successful use in this laboratory. It is very economical of solvent, requiring 0.2 kg. (0.5 pound) of ether for twenty determinations if no recovery is made.

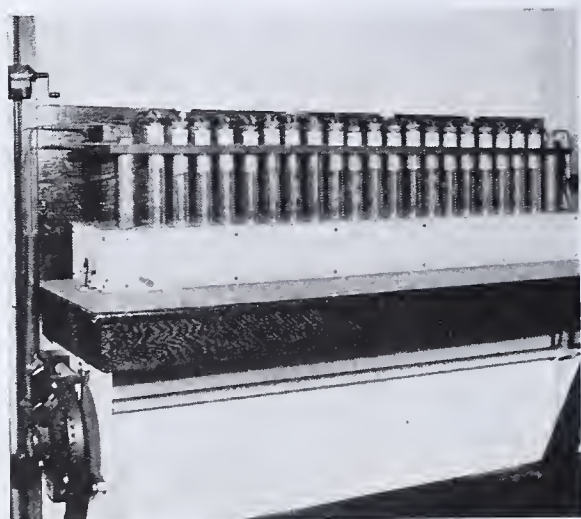


FIGURE 1. FAT-EXTRACTION APPARATUS

This unit consists of twenty large test tubes with an inside diameter of 35.5 ± 0.5 mm., and a length of 280 mm. each. Metallic zinc dust, wrapped securely in tin foil, is placed in the bottom of each tube to make the heat transfer more efficient and to eliminate the possibility of breakage when the fat container is placed in position. The condensers consist of test tubes with an outside diameter of 31.25 ± 0.25 mm. and a length of 115 mm. each. A short collar of 32-mm. heavy-wall rubber tubing supports the smaller test tube on the top of the larger one and a strip of tightly wound flannel about 25 mm. wide, just below the rubber ring, centers the condenser tube and aids in the complete condensation of the ether. Several layers of flannel strip are wrapped to such a thickness that the inner tube fits snugly into the outer one.

The outer tubes are heated in a copper water bath having twenty cups for the tubes and a copper tube condenser on each

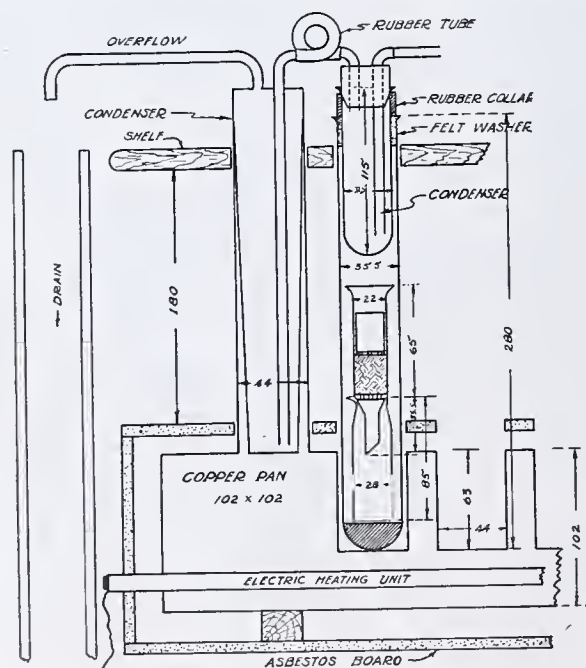


FIGURE 2. DETAIL OF APPARATUS
(All dimensions in millimeters)

end to keep the water level constant. The copper bath is covered with 6-mm. (0.25-inch) hard asbestos board supported on a 25-mm. (1-inch) wood frame, leaving a 25-mm. (1-inch) air space between the bath and the asbestos board cover, except on the top. Figure 2 shows one end of the setup in detail. The bath is heated by a 500-watt tubular, immersion water heater, and the temperature is controlled by a 25-cm. (10-inch) plate-type rheostat, having twenty-eight regulatory steps from 150 to 500 watts. The length of the asbestos-covered bath is 150 cm. (59 inches) with a front-to-rear depth of 26.5 cm. (10.5 inches), this depth being required for the rubber tubes which connect the condensers. Five ether condensers are cooled with one stream of water, making it necessary to have four water outlets, with needle valves, across the rear of the top shelf. The two waste overflows empty into drains at each end in such a way that the amount of water being discharged can be seen and the needle valves can be adjusted properly.

A constricted lipped container (length 85 mm., outside diameter 28 mm.) holds the ether and collects the fat. A funnel-top filter tube, 100 mm. long, rests on the top of the constricted fat container and is held upright by the funnel top. This filter tube holds the sample of feed and is made up as follows: A cupped perforated tin disk is placed in the bottom beneath a 10-mm. asbestos (acid- and alkali-washed and ignited) pad on which



FIGURE 3. ACCESSORIES

the feed is placed and then covered with a thin layer of asbestos (this asbestos layer together with a small amount of the bottom pad is removed with the feed for the crude fiber determination). A metal cup, made from a short piece of 13-mm. (0.5-inch) block tin pipe by soldering in a perforated bottom, rests on the asbestos layer. This holds the contents of the feed tube together, distributes the ether drip, and keeps the feed from raising up and channeling.

TABLE I. COLLABORATIVE RESULTS

Ether Extract	
West Virginia results	Average results of 53 laboratories
%	%
1.52	1.49
6.17	6.29
2.73	2.72
3.20	3.26
5.11	5.26
3.10	3.19
4.12	4.15
6.55	6.46
3.12	3.17
3.46	3.48
Av. 3.91	3.95

The results obtained by the use of this apparatus have been found to check those obtained by the use of the Soxhlet apparatus. Table I gives the results from 53 feed laboratories on check samples sent out by the Department of Agriculture in comparison with those obtained with this apparatus. The results show close agreement.

Figure 3 shows the accessories necessary for the operation

of the apparatus: a pair of straight-end tongs to remove and replace the metal cup, feed funnel, and fat flask; a straight funnel tube to add ether; an ether bottle with constricted tip for washing; a tin container with twenty places for the feed funnels, of such size as to fit a high-form 20.4-cm. (8-

inch) desiccator; and a tin container with twenty places for the fat flasks, of such size as to fit a 20.4-cm. (8-inch) desiccator.

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Lignin in Douglas Fir

The Pentosan Content of the Middle Lamella

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IN AN EARLIER communication (1) a method of isolating the middle lamella of wood was described. The isolated material was subsequently analyzed for lignin by a micro-method (2) developed for the purpose. The present report describes the analysis of another sample of middle lamella, which was isolated by the same method, in order to establish further the composition of the lamella by the identification of at least a portion of the unknown 29 per cent. As was pointed out earlier (1), several investigators produced evidence indicative of the presence of hemicelluloses in the middle lamella.

Methods of Hemicellulose Analysis

An inquiry into the prior work on hemicelluloses brought to light such an overwhelming mass of incomplete, contradictory, and apparently inaccurate information that there is little wonder that the nomenclature is so unsatisfactory. A brief but reasonably complete bibliography (3, 9-11, 17, 20-23, 27, 34) on hemicelluloses, including recent excellent reviews, offers a summary of present knowledge; hence it is unnecessary to epitomize the experimental work or to take up in detail the viewpoints of the various investigators. Inasmuch as the estimation of the hemicelluloses—rather than their constitution—was the primary consideration, only the analytical methods need discussion here.

Unfortunately, there is no method of making a complete analysis of hemicelluloses in a single sample. It is even impossible to define hemicelluloses in a way that has analytical significance. Supposedly, they are anhydrides of hexose and pentose sugars which are soluble in dilute alkalis and which are less resistant to hydrolysis by dilute acids than the remainder of the plant tissue. It is well known that these properties do not furnish a means of sharp distinction. There is no known method of determining the total hemicelluloses or the total hexoses in a single sample. Pentoses are usually determined by conversion to furfural, which may be estimated by oxidation or precipitation methods. Hexoses are usually determined by oxidation of the sugar or by conversion to the phenyl hydrazone or osazone (3, 18, 19, 30, 33-35). While the carbohydrates can be characterized fairly easily, their identification or quantitative separation from mixtures is exceedingly difficult.

An attempt to determine the total hemicelluloses was made by extracting a sample of wood with hot water, and then subjecting the residual wood to hydrolysis. The hot-water extractive of oven-dry Douglas fir (*Pseudotsuga taxifolia*) powder which had been put through a 100-mesh screen was 3.68 per cent; the subsequent loss in this sample, based on the original oven-dry weight of the wood, due to hydrolysis with 2 per cent sulfuric acid was 15.99 per cent; the loss in the extracted wood when refluxed with 2 per cent sulfuric acid was 27.15 per cent. On the basis of Schorger's definition,

that hemicelluloses are insoluble in hot water but are hydrolyzed by heating with dilute acids at atmospheric pressure (28), it would seem that the total hemicelluloses in Douglas fir constitute 16 per cent of the wood. That this is not accurate is shown by the fact that the extractive plus the loss by hydrolysis is greater than the loss by hydrolysis of the unextracted wood. In other words, the hot water alone either extracts some hemicelluloses or changes some constituents so that they are soluble in the dilute acid.

Further evidence that hemicelluloses are removed by hot water alone was found by an examination of the hot-water extractive. Treatment with phenylhydrazine and acetic acid in the cold yielded no mannose phenylhydrazone. When the hot water extract, however, was made up to a concentration of 5 per cent with hydrochloric acid, hydrolyzed, neutralized, and treated with phenylhydrazine and acetic acid in the cold, a small quantity of mannose phenylhydrazone was formed, together with a large quantity of an as yet unidentified compound with a melting point of 235° C. Hence, it may be concluded that mannan in Douglas fir is soluble in hot water but is not hydrolyzed by it. The total mannan by Schorger's method (12, 29) was found to be 5.33 per cent (Schorger found 6.65 per cent). After filtering off the mannose phenylhydrazone and other material from the hydrolyzate, heating in the presence of an excess of phenylhydrazine yielded the brownish yellow oily drops of the osazone of arabinose, phenylglucosazone, and another crystalline solid. When the hot-water extract, with no prior treatment, was made up to a concentration of 12 per cent with hydrochloric acid and distilled, the addition of thiobarbituric acid solution to the distillate produced furfuralmalonylthiourea. This fact extends earlier knowledge of the resistance of pentosans to hydrolysis to include not only those that occur in purified cellulose or those that are readily hydrolyzed by dilute acids, but also to those which are removed by hot water. In other words, hot-water extraction alone removes at least three hemicelluloses and other carbohydrates.

Likewise, there seems to be no way of determining the hexose hemicelluloses in a group in a single sample. Pentose hemicelluloses, however, can be distinguished easily from hexoses. Since the existing knowledge of hemicellulose chemistry was insufficient to permit an even reasonably complete determination, it was necessary to attempt to ascertain the hemicellulose most likely to occur in the middle lamella. Prior work pointed the way: Ritter and Fleck (25) found that the pentosan content of springwood was greater than that of summerwood. It was suspected that the higher volumetric fraction of lamella in the springwood was responsible. Other speculations (16), many of a teleological nature, however, had been voiced, showing the mechanism of chemical metamorphosis from pentoses to lignin, hence the possibility of a close relation between pentosans and the middle lamella.

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Since it was found earlier that the lignin content was higher in the springwood than in the total wood and even higher in the wood rays (1), check analyses were carried out, by a method described below, on ray tissue isolated by the micromanipulator to learn if this same pentosan-lignin association obtained. The pentosan content of the rays was found to be about 6.6 per cent, as compared to about 5.5 per cent for the total wood, or in linear relation to the lignin content. Accordingly, it appeared probable that the pentose hemicelluloses should constitute at least an important fraction of the total hemicelluloses and that their close and constant association with tissue which had both a high lignin content and a high volumetric fraction of middle lamella should assure their presence in the middle lamella in significant quantities.

Determination of Pentosans

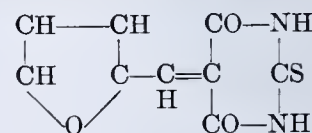
The determination of pentosans, for practical purposes, may be said to depend upon their conversion to furfural or methylfurfural, as the case may be, by distilling with a mineral acid of proper concentration and subsequent determination of the furfural by oxidation, precipitation by various reagents, by colorimetric means, or by other methods (23, 26). While the common method of determining pentosans consists of a strictly standard distillation and precipitation with phloroglucinol, many objectionable features are apparent. The distillation itself is not quantitative (7), while some furfural is destroyed by the high acid concentration during the latter part of the distillation (8). Furthermore, precipitation by phloroglucinol is not quantitative (8), necessitating a correction factor, while hydroxymethylfurfural, which is of hexose origin, is precipitated in small yield (24). The phloroglucide of furfural is not a compound of definite composition, varying with the temperature at which it is precipitated (32).

Virtually all objections may be overcome by proper modifications. By using the exceedingly accurate method of distillation with steam, first proposed by Jolles (15) and later modified by Pervier and Gortner (23), quantitative yields have been obtained from pure pentose materials (23). The accuracy seems to be due to the furfural's being swept out by the steam and to the constancy of acid concentration preventing destruction of the furfural. While many precipitants other than phloroglucinol have been used, only two merit attention. Barbituric acid was found to give nearly quantitative yields as a precipitant for furfural without precipitating hydroxymethylfurfural (7, 24, 31). Dox and Plaisance (4) found that thiobarbituric acid gave quantitative or slightly better yields, that only a slight excess of the precipitant was necessary thus avoiding the danger of inclusion, that it was very sensitive to exceedingly small amounts of furfural, and that the precipitate was a compound of definite and uniform composition—namely, furfuralmalonylthiourea. Other investigators found that thiobarbituric acid precipitates both furfural and methylfurfural quantitatively and that while it reacts with hydroxymethylfurfural, the resulting product is soluble, coloring the solution, but not interfering with the determination of pentoses (5, 31). The superiority of thiobarbituric acid over phloroglucinol has been verified by the researches of other workers (24, 26). It appeared, therefore, that the most promising method for the determination of pentoses in microquantities was to reduce the method of steam distillation of Pervier and Gortner and to use thiobarbituric acid as the precipitant.

PROCEDURE. On a macrobasis high precision was obtained on samples of 100-mesh (rasped and passed through a 100-mesh screen) oven-dry wood ranging in size from 0.1 to 3.0 grains. One modification of the Pervier and Gortner method increased the precision and shortened the time—viz., the

substitution of a 125-ml. flask for the 750-ml. distilling flask and the addition of 50 ml. of 12 per cent hydrochloric acid instead of 200 ml. The increase in precision was presumably due to better contact of steam and furfural. In distilling, a moderate stream of steam was passed in at a constant rate throughout the distillation and the temperature, as measured by a thermometer in the vapor in the neck of the flask, was maintained between 103° and 105° C. by boosting the distilling flask with a burner. Distillation was continued until a small sample of the distillate in thiobarbituric acid solution gave no precipitate or turbidity after standing 5 minutes. The value of aniline acetate paper (or hydrochloride) as an indicator, while entirely satisfactory on pure pentose material, was found to be worthless on wood, since the hydroxymethylfurfural from the cellulose, etc. (13, 14), reacted with the thiobarbituric acid as Unger and Jäger pointed out (31), giving a colored compound which was also found to be the case with both the papers and solutions of aniline salts. In thiobarbituric acid solution, however, the difference between a color and turbidity could be easily detected, thus providing a simple and accurate means for determining the end of the distillation. Pervier and Gortner found their method of distillation to give theoretical yields of all pure pentose materials.

Thiobarbituric acid was obtained from the Eastman Kodak Company and was prepared by the method of Gabriel and Coleman (6). Both gave satisfactory results. The furfural was precipitated from the distillate by adding a slight excess of thiobarbituric acid in 12 per cent hydrochloric acid at room temperature and allowing to stand overnight. The lemon-yellow compound formed was filtered on a tared Gooch crucible, dried at 105°, and weighed as furfuralmalonylthiourea:



which is uniform and constant in composition (4). Values obtained in the presence of methylfurfural are only very slightly in error, because the molecular weight of the residue is between furfural and methylfurfural. Calculations were based upon the following relations:

$$\begin{aligned} \text{Pentosan} &\longrightarrow \text{furfural} + 2 \text{H}_2\text{O} \\ \text{Weight of furfural} &= \frac{\text{furfural} + 2 \text{H}_2\text{O}}{\text{furfuralmalonylthiourea}} = 59.6 \end{aligned}$$

Microdetermination of Pentosans

A microprocedure was developed which is as follows:

A 6-ml. flask was blown from tubing having an inside diameter of 9 mm., and a long side tube was sealed on the neck of the flask. A tube larger than the side tube was fitted with two side tubes to form the outer condenser shell, and slipped sleeve-wise over the long side tube of the flask, which formed the inner condenser shell. The ends of the outer tube were then made tight with rubber tubing, thus providing a means of condensation in the side tube of the flask and eliminating all joints from the system. Another flask of the same size was blown for the steam generator and connected to the distilling flask by small-bore tubing. A microthermometer was made by blowing a bulb on a capillary tube, filling it with an alcoholic solution of safranin, and sealing. It was calibrated in a thermostat at 103° and 105° C.

The distillation was conducted in the same manner as in the macroprocedure, samples in each case being introduced into the flask in small glass boats and the flask being filled half full (50 ml. in the macro- and 3 ml. in the microprocedure) of 12 per cent hydrochloric acid. In the microprocedure the boat was first dried at 105°, cooled in a desiccator, then placed in a weighing bottle kept in the balance case, and weighed. This process was repeated with a sample in the boat in order to obtain identical anhydrous surface conditions on the glass boat without error due to hygroscopicity. The same technic was used in weighing the

micro-Gooch crucible. Samples of approximately 3 mg. of wood were used in the microprocedure.

Results of Pentosan Analyses

Table I summarizes the results of analyses by macro- and microprocedures. The analysis of a single sample of the middle lamella weighing 1.127 mg. showed a pentosan (including methylpentosan) content of 14.21 per cent. Subsequent filtration and chlorination of the residue showed a cellulose content of 4.1 per cent.

TABLE I. PENTOSAN CONTENT OF DOUGLAS FIR

A ^a	B ^b	C ^c	D ^d
4.53	5.38	5.46	6.61
4.69	5.53	5.62	6.45
4.53	5.43	5.54	6.78
4.61	5.41	5.35	6.71
4.58	5.49	5.41	6.49
4.65	5.46	5.50	6.58
Av. 4.60	5.45	5.48	6.60

^a A, total wood sawdust by macroprocedure.
^b B, 100-mesh total wood by macroprocedure.
^c C, 100-mesh total wood by microprocedure.
^d D, ray tissue by microprocedure.

Significance of Pentosan Analyses

The difference between sawdust and 100-mesh wood is typical of many wood analyses, the results depending upon the degree of subdivision of the sample. The precision of the micromethod shown in C and D, Table I, probably obtained in the analysis of the middle lamella, as the quantity of furfuralmalonylthiourea obtained was approximately the same in each case. Ritter and Fleck (25) showed both the lignin and pentosan content of springwood to be about 10 per cent greater than in the summerwood. It has been shown above that both the lignin and pentosan content of the rays were about 20 per cent greater than in the total wood, and by analysis of the middle lamella that the lignin and pentosan content in the latter tissue was 215 and 260 per cent greater, respectively, than in the total wood. While this clear-cut relation between lignin and pentosan content and their constant association may be entirely accidental, it is equally possible that these data point to the origin of lignin. Schorger (12, 29) and Ritter and Fleck (25) found the pentosan content of Douglas fir to be nearly double that found above for the total wood. While their results are in good agreement with each other, the phloroglucinol method which was employed to obtain these results has been shown to be greatly in error by Gierisch (7, 8), Heuser and Stöckigt (14), Pervier and Gortner (23), Peter, Thaler, and Täufel (24), Unger and Jäger (31), and Votoček (32).

Summary of Middle Lamella Composition

The small quantity of cellulose present in the isolated sample of middle lamella affords an accurate index of the extraneous material which was unavoidably included in the isolation. The composition of the middle lamella may be summarized as follows: lignin 71 per cent, pentosans 14 per cent, unknown 15 per cent. The 4 per cent of cellulose in the isolated sample probably should be regarded as the error in isolation. If this be done, the values for lignin and pentosan are slightly low. There is no reason to believe that the composition of the middle lamella is uniform in different species and genera or even in the same species. The association of lignin and pentosans in nearly direct relation suggests, but offers little conclusive evidence, that pentoses antecede lignin. Such association is difficult to interpret on the basis of present knowledge of wood chemistry. The fact that pentosans may be present in the middle lamella necessitates modifications in present opinions of both chemical and botani-

cal investigators as to the cause and significance of solubility and staining reactions of the middle lamella. It appears that the major contribution of these findings, at the moment, has fundamental rather than practical importance.

Summary

This paper describes a continuation of the analysis of the middle lamella which was isolated mechanically by a micro-manipulator in order to determine the pentosan content of the middle lamella. Methods of hemicellulose analysis are discussed and data on hemicelluloses in Douglas fir reported. An accurate gravimetric method of determining pentosans by steam distillation and precipitation of the furfural by thiobarbituric acid is suggested. The procedures for the determination of pentosans on both macro- and microsamples are outlined and the precision of each is indicated. An isolated sample of middle lamella of Douglas fir showed a pentosan content of 14.21 per cent (the first paper describing this work indicated a lignin content in the middle lamella of 71 per cent). A direct and nearly constant relation between lignin and pentosan content was found in different wood elements. This suggests that pentoses take part in the formation of lignin, although the indicia are circumstantial. The importance of the findings is discussed.

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Separation and Determination of Bismuth with Gallic Acid

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GALLIC acid as a reagent for the precipitation of bismuth was used in qualitative analysis by Das-Gupta (1), but apparently no investigation of the quantitative possibilities was made. In view of the small number of ions forming precipitates with gallic acid, it seemed worth while to determine what separations of bismuth from other elements were possible.

Reagents

The bismuth nitrate solution used was prepared from Bureau of Standards metallic bismuth and Baker's analyzed acid. A 3 per cent nitric acid solution was used. The acid concentration in all work is expressed in percentage by volume. The gallic acid was Kahlbaum's D. A. B. No. 5 grade.

Procedure

The 3 per cent bismuth nitrate solution containing the other elements was heated to 70° C., 50 cc. of gallic acid (1 gram of solid reagent) were added, and the solution was stirred for 1 minute. The solution was allowed to cool before filtering. The clear liquid was poured through the filter and the precipitate washed by decantation with 150 cc. of a solution containing 2 grams of gallic acid and 3 grams of ammonium nitrate per 100 cc. of water. The filter paper was transferred to the original beaker, 20 cc. of nitric acid were added, and the mixture was heated to dissolve the precipitate and break up the filter paper. The paper pulp was filtered and washed with 200 cc. of a 5 per cent nitric acid solution to free it from bismuth. The solution was evaporated to dryness and 10 cc. of nitric acid with 50 cc. of water were added. In order to separate bismuth from the other elements, a reprecipitation is necessary; consequently ammonium hydroxide was added until the solution was basic, then nitric acid to make it just acid. The solution was heated to 70° C. and the bismuth reprecipitated with gallic acid. The same procedure as described above was then used up to the point at which ammonium hydroxide was added. At this point the bismuth was precipitated as the subcarbonate and ignited to the oxide (2).

The results are given in Tables I, II, and III.

Certain details of the above procedure require mention: (1) At a temperature above 85°, gallic acid starts to decompose and among the products some compound, the exact composition of which is unknown, prevents the complete precipitation of bismuth. (2) It is necessary to evaporate to dryness in order to destroy any decomposition products of gallic acid; otherwise complete precipitation of the bismuth cannot be obtained. (3) Because of the ease with which bismuth compounds are reduced to the metal, the bismuth gallate could not be ignited to the oxide.

Interfering Elements

Mercury and antimony are precipitated partially with gallic acid. Tin interferes because it hydrolyzes in a 3 per cent acid solution. Silver cannot be removed with two precipitations.

Summary

Bismuth can be separated and determined in 3 per cent nitric acid solution in the presence of lead, cadmium, copper, zinc, aluminum, chromium, iron, nickel, barium, calcium, sodium, and potassium. Bismuth cannot be separated from antimony, mercury, tin, and silver.

TABLE I. SEPARATION OF BISMUTH

Bi ₂ O ₃ Taken Gram	Pb Present Gram	Cd Present Gram	Bi ₂ O ₃ Found Gram	Difference
Separation from Cadmium and Lead				
0.1120	0.083	0.04	0.1117	-0.0003
0.1120	0.083	0.04	0.1118	-0.0002
0.1120	0.083	0.04	0.1118	-0.0002
0.1120	0.083	0.04	0.1118	-0.0002
0.1120	0.083	0.04	0.1121	+0.0001
Separation from Aluminum and Copper				
	Al Present	Cu Present		
0.1120	0.05	0.05	0.1116	-0.0004
0.1120	0.05	0.05	0.1118	-0.0002
0.1120	0.05	0.05	0.1117	-0.0003
0.1120	0.05	0.05	0.1117	-0.0003
0.1113	0.05	0.05	0.1110	-0.0003

TABLE II. SEPARATION OF BISMUTH

Bi ₂ O ₃ Taken Gram	Cr Present Gram	Bi ₂ O ₃ Found Gram	Difference
Separation from Chromium			
0.1120	0.0312	0.1123	+0.0003
0.1120	0.0312	0.1121	+0.0001
0.1120	0.0312	0.1118	-0.0002
0.1120	0.0312	0.1117	-0.0003
0.1120	0.0312	0.1121	+0.0001
Separation from Nickel			
	Ni Present		
0.1120	0.075	0.1118	-0.0002
0.1120	0.075	0.1120	0.0000
0.1120	0.075	0.1122	+0.0002
0.1120	0.075	0.1121	+0.0001
0.1120	0.075	0.1120	0.0000
Separation from Zinc			
	Zn Present		
0.1113	0.08	0.1110	-0.0003
0.1113	0.08	0.1111	-0.0002
0.1113	0.08	0.1111	-0.0002
0.1113	0.08	0.1111	-0.0002
0.1113	0.08	0.1113	0.0000
Separation from Iron			
	Fe Present		
0.1113	0.01	0.1117	+0.0004
0.1113	0.01	0.1112	-0.0001
0.1113	0.01	0.1110	-0.0003
0.1113	0.01	0.1110	-0.0003
0.1113	0.01	0.1112	-0.0001

TABLE III. SEPARATION FROM SODIUM, POTASSIUM, CALCIUM AND BARIUM

Bi ₂ O ₃ Taken Gram	Na Present Gram	K Present Gram	Ca Present Gram	Ba Present Gram	Bi ₂ O ₃ Found Gram	Difference
0.2801	0.09	0.08	0.08	0.08	0.2798	-0.0003
0.2801	0.09	0.08	0.08	0.08	0.2799	-0.0002
0.2801	0.09	0.08	0.08	0.08	0.2797	-0.0004
0.2808	0.09	0.08	0.08	0.08	0.2809	+0.0001

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A Simple Portable Aradiant Convection Pyrometer

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ALTHOUGH radiation errors in the measurement of temperature of gases are common and frequently of comparatively great magnitude, correction for these errors is at best a rough approximation and involves considerable inconvenience. This is due to the lack of sufficient data on emission coefficients and the difficulties met in accurately measuring the temperature of all surfaces which may be radiating heat to or receiving heat from a static thermocouple. It is evident that the development of a convenient form of pyrometer for measuring the true temperatures of gases without the necessity for attempting corrections is much needed.

Various suggestions for eliminating the effect of radiation on pyrometer readings have been made. Methods of shielding the measuring element from radiation from the walls by means of polished metal surfaces and the use of a shield with regulated temperature have been described (4). Heat-insulating shields have also been suggested, and the use of small measuring elements has been investigated (5). This latter method partially accomplishes the desired radiation correction because radiant heat transfer takes place at the surface of the element while transfer of heat by convection takes place at the surface of a stagnant film around the measuring element and of greater area than the element. For very small elements it is obvious that this difference in heat transfer area may become proportionately large. These methods, however, are accurate only under a comparatively narrow range of conditions and are not so generally applicable as to lead to the development of a convenient portable temperature-measuring instrument.

It was early experimentally discovered that the velocity of the gas past the pyrometer element affected the reading and that a higher speed decreased the error due to radiation (12). In nearly all measurements of gas temperature, heat from the substance whose temperature is to be measured is transmitted to the measuring element by convection only. It is, therefore, advantageous to use methods which increase the heat transfer by convection as well as decrease that by radiation. The use of suction to increase the velocity of the gas past the thermometer element accomplishes this, since the coefficient of heat transfer increases with the velocity of the gas past the heat-transfer surface (10). Several attempts to apply this principle have been made (1-3, 6-9, 11), but none of these so-called "high velocity" thermocouples or "suction" pyrometers has been developed into an instrument which is of general utility and is still dependable and easily handled. Most are unwieldy and lack sufficient simplicity in construction to be widely used.

The design of the proposed instrument should embody the following features: The gas velocity past the measuring element should be sufficiently large to make heat transfer by radiation an insignificant part of the total amount; likewise, leads from the element should be so small that conduction along them is negligible. The high gas velocity must be obtained by the diversion of the smallest feasible amount of the gas from its normal path. Cooling the gas before reaching the

suction mechanism may be necessary. To reduce radiation, an insulating shield should be placed around the element. Any type of element may be used, providing it registers by conduction and its impulses can be transmitted by leads; this limits the selection, for practical purposes, to the thermocouple, although the resistance thermometer element might be used. Finally, all parts should be small, to allow use in cramped quarters, and as light as consistent with structural and thermal strength.

Design of Instrument

The instrument developed has been made in two forms, diagrams of which are shown in Figure 1. Each has certain constructional advantages, but neither construction involves the sacrifice of any desired characteristics of performance.

The first was built up from standard parts obtainable from any laboratory supply house. A 28-inch length of 0.375-inch copper tubing was flared and fitted with a T-fitting at one end and a standard coupler at the head. The thermocouple leads were carried from the head in standard 0.1875-inch two-hole alundum insulators placed inside the copper tube. The thermocouple junction itself was fused to a small bead and placed in the center of a 0.0938-inch hole in a slate disk cut for the purpose and held in position by the cap and asbestos packing placed over it. An inlet hole 0.3125 inch in diameter was drilled in the cap. To help

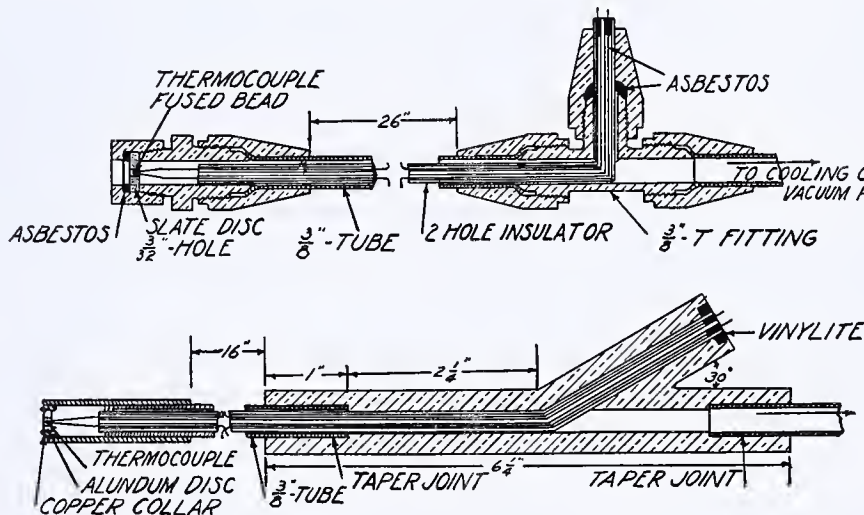


FIGURE 1. TWO TYPES OF ARADIANT CONVECTION PYROMETER

prevent the effects of conduction of heat along the lead wires, they were left unsupported for the last 0.75 inch. The alundum tubing was fixed at the center of the copper tube by crimping the end at 3 points. The lead wires were carried out through the T-fitting. This point had the alundum insulator packed in with asbestos and the holes filled in with high-temperature cement to prevent air leakage. To the remaining end of the T-fitting was attached a 7-inch double coil of the same size tubing, which served to cool the gases before they reached the pump.

The second design was the result of a suggestion by Harry McCormack, Department of Chemical Engineering, Armour Institute of Technology, Chicago. In this design all screwed couplings were eliminated and taper joints substituted. The T-fitting in the first design was replaced by a special brass casting with the angle changed to 30°. The thermocouple was carried as before in 0.375-inch copper tubing, but the coupling at the head was replaced by a 1.75-inch length of 0.5-inch copper tube. The disk in this case was cut from standard 0.25-inch alundum single-hole insulator and was held in a 0.1875-inch length of 0.375-inch tubing whose ends were rolled in. This assembly was a force fit in the 0.5-inch tube. The three main joints were made

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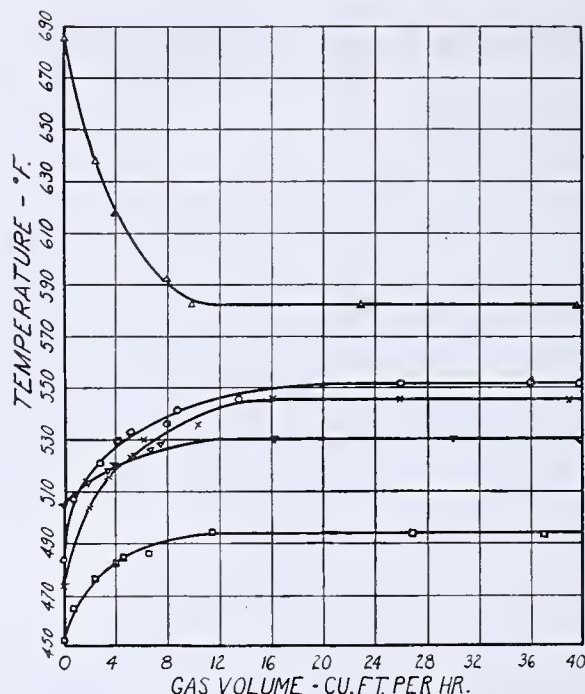


FIGURE 2. TYPICAL CALIBRATION CURVES

by machining the 0.375-inch copper tube for a taper fit, 0.1875 inch taper per foot being used. A 7-inch double cooling coil was fitted as before. The lead wires were sealed at their point of exit by counterboring for 0.125 inch and filling with vinylite which was baked in.

This design has the advantage of very small size at the head, the greatest outside diameter at that point being 0.5 inch. The heads of both instruments are small, however, so they may be used in the determination of temperatures in large spaces or as a probe between the sections of a pipe coil. For use with temperatures higher than copper will stand, a large variety of metal tubings is available. Since the gases are cooled practically to room temperature, it is possible to use any convenient pumping device, from a laboratory vacuum pump to a steam ejector, with rubber tubing as the connector.

In an experimental gas-fired furnace, tests on the reliability of the apparatus described were made. A small laboratory rotary vacuum pump was used as the source of vacuum, and a Leeds & Northrup student potentiometer, with chromel-alumel thermocouple, giving readings accurate to 1°F. , was used to measure the temperature. In all cases equilibrium temperature was reached when the rate of gas flow was 12 cubic feet per hour, and in some cases the necessary amount of gas to be removed from the furnace was only 8 cubic feet per hour.

Discussion

Graphs of the effect of gas velocity on the approach to true temperature are shown in Figures 2 and 3. These results, of course, apply only to this instrument and in the general case are qualitative only. The size of the bead and thermocouple junction, the diameter and length of the lead wires, and the capacity of the source of vacuum used, all affect the accuracy of the temperature reading, as does the main source of radiation error, the difference in temperatures of the gas and the radiant solid surfaces to which the pyrometer element is exposed. Since any method of accurate gas temperature measurement involves only the reduction of radiant heat transfer to the measuring element and increase of flow by conduction and convection, the temperature indicated will approach the true temperature asymptotically, but will never entirely reach it. The accuracy of the method depends, finally, on how far it is possible or convenient to carry this convergence toward the asymptote.

Structurally, the accuracy of the aradiant convection pyrometer depends primarily on the design of the head. The pyrometer may be made as sensitive as desired by decreasing

the size of the thermocouple bead while maintaining the necessary linear gas velocity. Too great sensitivity is in many cases undesirable, however, the averaging effect of the less sensitive head making the use of the pyrometer data much less complex. Thus, in the experimental gas-fired furnace used in this work, a sensitive head showed irregular temperature oscillations with amplitudes of more than 50°F. and periods of the order of 1 second, at temperatures about 700°F. Furthermore, displacement of the head by less than 0.5 inch produced a variation of 50°F. in an otherwise essentially constant temperature. Such sensitivity would be excellent in an instrument designed to study drafts and eddy currents in a furnace, but the automatic averaging effect of the larger bead is more desirable in making heat balances and heat-transfer studies. The pyrometer may be very effectively used to take gas samples while making the temperature readings.

While a high linear gas velocity is desirable for the purpose of increasing the rate of heat transfer between the measuring element and the gas whose temperature is to be measured, this same high velocity will also tend to promote heat transfer between the gas and portions of the head of the instrument, the temperatures of which are affected by radiation, thus introducing error. This was found to be the case in instruments in which the thermocouple bead was placed in an alundum capillary tube of any length. The temperature of the gas passing at high velocity through the capillary would tend to approach that of the refractory material, which in turn was greatly affected by radiation. This was shown by the high

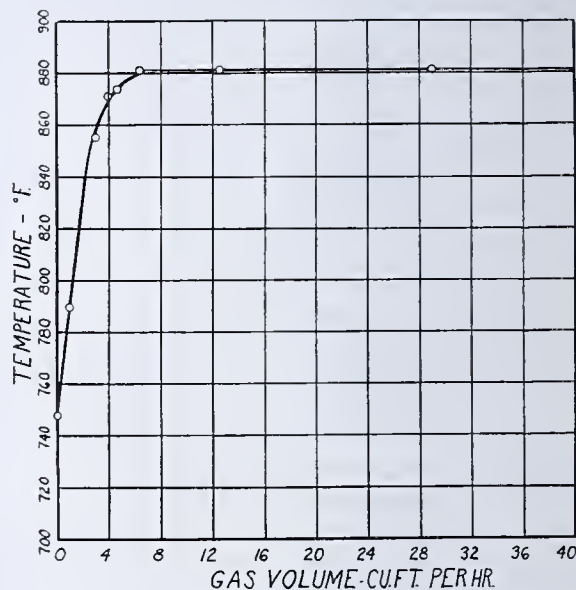


FIGURE 3. TYPICAL CALIBRATION CURVE

lag in some of the instruments. However, the substitution of a refractory disk drilled to give the proper gas velocity, with the thermocouple bead placed directly behind the hole, gave excellent results. Constant temperature was attained after a lag of only 1 to 2 seconds in this type of instrument. Upon removal from the furnace the reading would immediately drop to room temperature, although the head of the instrument remained hot. Shutting off the gas flow resulted in an immediate increase in reading, caused by conduction from the heated head. Resumption of the gas flow caused the reading to drop to room temperature again.

The aradiant convection pyrometer was tested for radiation errors by pointing the instrument in a direction such that the element was exposed to radiation from the back of a muffle furnace at bright red heat. No change in reading was perceptible when the source of radiation was covered and uncovered.

The terms "high-velocity" thermocouple and "suction" pyrometer have previously been applied to this type of instru-

ment. Neither of these appellations is satisfactory; neither is sufficiently descriptive of the purpose and the first is in some ways actually misleading. Since the instrument is expected to minimize the effect of radiant energy absorption and increase the transfer of heat by convection, and since the principle is applicable to at least two different types of measuring elements, it is suggested that such a piece of equipment be termed an aradiant convection pyrometer.

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Laboratory Gas-Absorption Vessels

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THE gas-absorption vessels shown in Figure 1 were developed after considerable experimentation with various types of absorbers. They operate on the same principle as the absorbers designed by Weaver and Edwards (8), Milligan (7), Beaumont, Willaman, and De Long (1), and Harvey and Regeumbal (3), but in certain respects are perhaps better adapted for general laboratory use.

Gas Scrubber

Apparatus A is a convenient and efficient gas scrubber designed to supply a continuous stream of purified air or other

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gas wherever needed in the laboratory. It has been found especially useful in preparing large volumes of carbon dioxide-free distilled water by the aspiration method. When used for this purpose, the stream of carbon dioxide-free air supplied from the scrubber is dispersed in the water by means of a sintered-glass distributing disk which may be prepared by the methods described by Kirk, Craig, and Rosenfels (5), and Cool and Graham (2). The carboy aspiration assembly is shown in C. The air may be forced through the system by either compression or suction, the latter usually being preferable when the aspiration is allowed to run overnight, or when compressed air is not readily available. The efficiency with which carbon dioxide is removed from water by this method

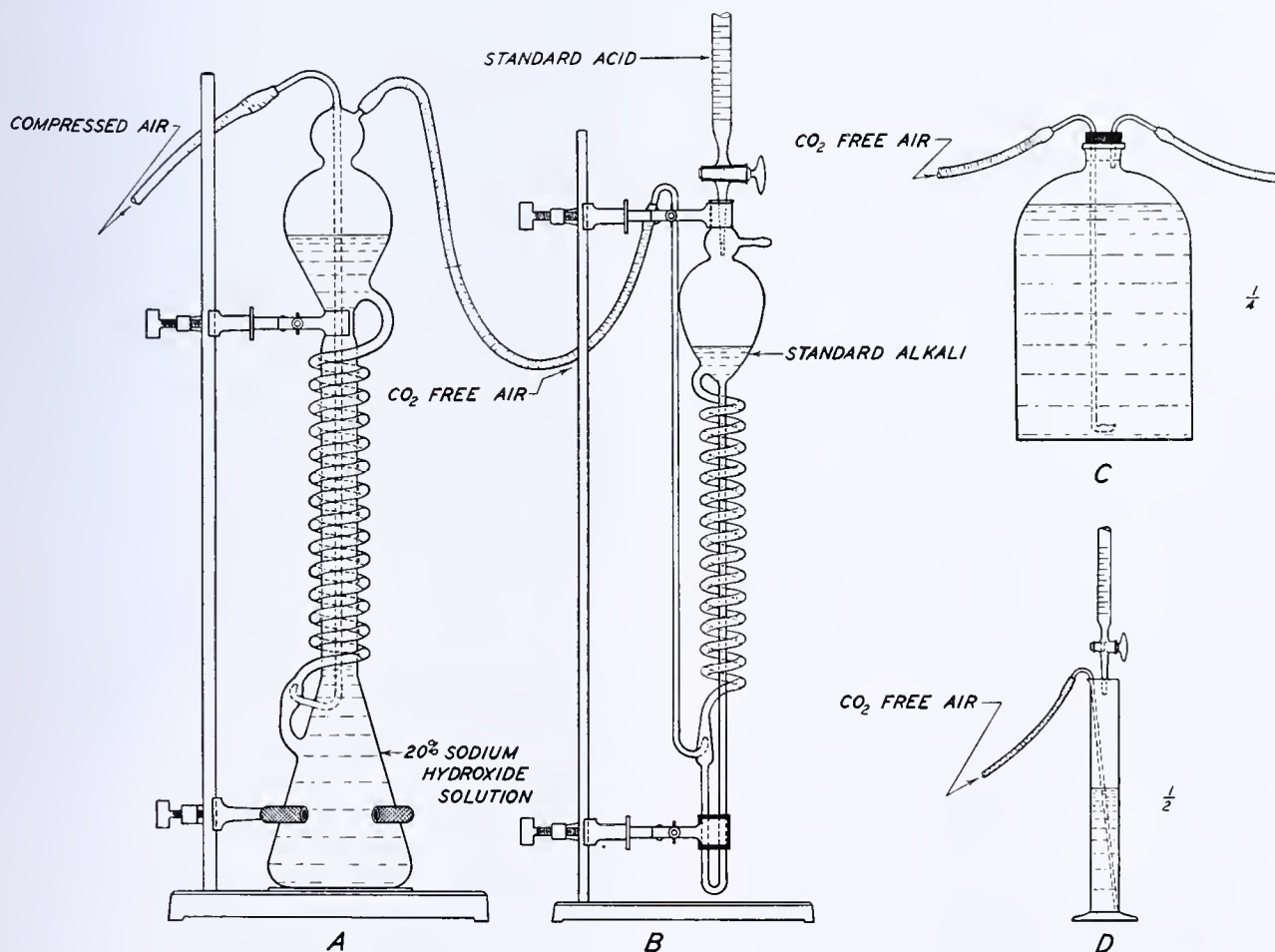


FIGURE 1. APPARATUS

- A. Laboratory gas scrubber.
- B. Quantitative gas-absorption vessel in which absorbing solution is titrated directly; a current of carbon dioxide-free air being used to stir and circulate the solution in the vessel during titration.

- C. Removal of carbon dioxide from a carboy of distilled water by aspirating with a current of carbon dioxide-free air.
- D. Assembly for stirring solution with a current of carbon dioxide-free air during titration.

is obviously determined by the rate of aspiration, the degree of dispersion of the gas stream, and the length of the path of the gas bubbles through the liquid. Using a small water pump of the usual laboratory type, adjusted to draw a gentle stream of air through the system, a 40-liter carboy of distilled water is rendered carbon dioxide-free overnight, or in from 12 to 16 hours. Following aspiration, the inlet to the distributing tube is closed with a pinchcock and the outlet connected to a soda-lime trap, the carbon dioxide-free water being withdrawn as needed through a siphon tube not shown.

The scrubber may also be used to supply a current of carbon dioxide-free air to stir solutions which are affected during titration by carbon dioxide or other reactive atmospheric gases. The stream of purified air not only stirs the liquid during titration and thus permits the operator to observe more closely the approach of the end point, but it also sweeps the atmosphere above the liquid free from carbon dioxide and other interfering gases, thereby obviating errors which inevitably occur when alkaline solutions are exposed to the atmosphere. Although any form of titration vessel may be used, the stirring action is most effective in a cylindrical vessel similar to that shown in *D*. The solution to be titrated is put into the vessel in a countercurrent of carbon dioxide-free air for the reasons already mentioned.

Many other uses may be found in chemical and physical laboratories for a gas scrubber of the type herein described. For example, it may be used not only for purifying gas streams, but also for drying or controlling their moisture contents at any desired degree of saturation. For the latter purpose, the scrubber may be charged with concentrated sulfuric acid, sulfuric acid solutions, or saturated solutions of certain salts (4). When the saturated salt solutions are used in the presence of an excess of the solid salt, a gas stream may be maintained at a constant degree of saturation continuously over long periods. The scrubber is easily charged with the excess salt by filling it with a hot saturated solution and then allowing it to cool, the amount of salt crystallizing from the solution being determined by the temperature at which the solution is saturated. To prevent closure of the tubes by the crystallizing salt during cooling, air is drawn into the spiral from the inlet jet, after which the outlet tube is closed with a pinchcock. As cooling proceeds, an occasional bubble of air is drawn into the system through contraction, thus keeping the inlet orifice open. The crystallizing salt settles to the bottom of the apparatus where the solution is continually circulated in contact with it to maintain a state of saturation. Obviously, the volume of gas which may be treated without recharging the apparatus will depend on its moisture content and on the quantity of undissolved salt, the latter going into solution when the partial pressure of the water vapor of the gas stream is greater than that of the saturated solution, and crystallizing out when it is less.

For general laboratory use, the following dimensions (outside measurements) have been found very satisfactory, but if desired the apparatus may be constructed with larger reservoirs to increase its capacity.

DIMENSIONS OF LABORATORY GAS SCRUBBER A

Height of apparatus, cm.	65
Upper reservoir:	
Height, cm.	12
Diameter, cm.	10
Volume (capacity), ml.	500
Lower reservoir:	
Height, cm.	20
Diameter, cm.	13
Volume (capacity), ml.	1000
Cylindrical tube connecting upper and lower reservoirs:	
Height, cm.	25
Diameter, cm.	3.5
Helical tube:	
Length, cm.	200
Diameter, cm.	0.6
Inlet jet, diameter of orifice, cm.	0.1
Aspiration rate, liters per hour	75

Absorption Vessel

Apparatus *B* is a quantitative absorption vessel in which the absorbing solution is titrated directly, thus obviating the errors which inevitably occur when aliquots are removed for titration. This is an especially important consideration in titrating alkaline solutions to an alkaline end point. The gas to be determined is passed through the apparatus charged with the absorbing solution, which is then titrated by connecting the absorber to scrubber *A* as shown. The stream of carbon dioxide-free air effectively stirs the solution and circulates it in the absorber during titration, while at the same time the countercurrent of air prevents carbon dioxide and other interfering atmospheric gases from diffusing into the vessel. Either compression or suction may be used to force the air through the system. If the latter is used, the tip of the buret is inserted through a rubber stopper (not shown) fitted into the tubulure at the top of the absorber. The dimensions (outside measurements) of the various parts of the apparatus are as follows:

DIMENSIONS OF QUANTITATIVE ABSORPTION VESSEL B

Height of apparatus, cm.	60	Spiral tube:	
Reservoir:		Length, cm.	180
Height, cm.	11	Diameter, cm.	0.6
Diameter, cm.	8	Inlet jet:	
Volume capacity, ml.	300	Diameter of lead-in tube, cm.	0.4-0.5
Vertical tube:		Diameter of orifice, cm.	0.05
Length, cm.	42	Aspiration rate, liters per hour	20-25
Diameter, cm.	0.6		

The aspiration rate given is for the complete absorption of CO_2 in 0.1 *N* barium hydroxide solution. Obviously, the efficiency of absorption is dependent on the concentration of the absorbing solution as well as on the aspiration rate.

The principal advantages of the above absorber over most of those in general use are its efficiency in absorption, its small capacity for absorbing solution, and its design which permits direct titration of the absorbing solution without removing it from the vessel. Inasmuch as it will operate on as little as 30 ml. of liquid, relatively concentrated absorbing solutions may be used without requiring inconveniently large volumes of standard solution in titration. The importance of this feature has been discussed by Martin and Green (6) in their studies on the efficiency of absorption of carbon dioxide by barium hydroxide solutions of different concentrations. Although originally designed for the determination of carbon dioxide in respiration studies, it has been found highly satisfactory for the determination of free and combined ammonia by the aspiration method. The ease with which the absorbing solution may be titrated in the vessel makes it especially suitable for the determination of ammonia nitrogen in soils and similar material.

Both gas-absorption vessels were made in a commercial glass-blowing laboratory operated by Mr. Greinke, Physics Department, University of Minnesota.

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An Analysis of Alkyd Resins

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AS THE oil-modified polyhydric alcohol-polybasic acid resins (hereafter called alkyd resins) come into more general use, methods for their analysis will be needed by the paint chemist and others who must know their composition.

A search of the available literature did not reveal a method for the analysis of alkyd resins. The method given below is a modification of an outline of a method suggested for use in examining alkyd resins to be submitted under specification for use on naval aircraft (Naval Department Specification V-11 for glyceryl phthalate aircraft spar varnish, Naval Aircraft Factory, Philadelphia, Pa.), in which conditions are not defined precisely enough so that results can be reproduced. The method is based upon the fact that acid can be added in proper amount to the saponified resin to free all the fatty acids without liberating any phthalic acid; the fatty acid can be removed by extraction with ether; and the phthalic acid can be freed by addition of more acid and removed by extraction with ether.

Method of Analysis

In the analysis of a resin, remove the pigment, if present, by means of a supercentrifuge. Put from 10 to 20 grams of the clear resin solution into a weighing bottle made from a 30-ml. Erlenmeyer flask fitted with a cork through which is inserted a medicine dropper.

ASH. Determine the amount of ash and the identity of the metals in it from this solution. The ash of a perfectly clear sample may be as much as 3 per cent of the solids. If the ash is as much as 0.1 per cent of the solids, subtract it from the per cent of solids to get the per cent of resin. This correction is not very precise but it is better than no correction. If the composition of the drier is known, a more precise correction can be made.

PER CENT OF SOLIDS. To determine the percentage of solids, transfer 1 to 1.5 grams of solution to each of two shallow pans 4 to 5 cm. in diameter. Heat the pans at 105° C. for 2 hours and weigh. Heat the pans an hour longer and weigh again. If the changes in weight are less than 1 mg., or if the percentages of solids are within 0.05 per cent of each other, then calculate the per cent of solids from the weight of the resin left after 3 hours heating. If the changes in weight are large or the percentages of solids do not agree within 0.05 per cent, heat longer, and weigh at half-hour intervals until the weights are constant or until there is an increase in weight due to oxidation of the oil. Use the minimum weight of the resin to calculate the percentage of solids. Usually the resin solutions are between 40 and 80 per cent solids.

Acid Number, Oil, and Phthalic Anhydride

The acid number, oil, and phthalic anhydride are determined on the same sample. It is convenient to report the results as percentage of glyceryl phthalate and oil in the solid resin, even though they may not exist as such in the resin.

ACID NUMBER. The acid number is the number of milligrams of potassium hydroxide which must be added to 1 gram of resin to neutralize it to the phenolphthalein end point.

Weigh 0.75 to 1.0 gram of resin (1 to 2 grams of resin solution) into each of two 250-ml. Erlenmeyer flasks, add 25 ml. of benzene and 25 ml. of alcohol (95 per cent) and a few drops of phenolphthalein, and titrate with aqueous 0.1 *N* potassium hydroxide until the pink color develops. If the acid number is greater than 15, the end point will be indefinite and the observed value for acid number low. In this case, determine the acid number on a separate sample dissolved in 50 ml. of acetone. Naphthenate driers may increase the acid number several units.

A method is described for the analysis of alkyd resins. The method is based upon the fact that acid can be added in proper amount to the saponified resin to free all the fatty acid without liberating any phthalic acid; the fatty acid can be removed by extraction with ether; and the phthalic acid can be freed by addition of more acid and removed by extraction with ether. Specific directions for performing the analysis are given.

OIL. To each flask, after the acid number determination, add 10 ml. of aqueous 6 per cent potassium hydroxide solution to saponify the resin. Place an air condenser in the neck of the flask, and heat on a hot plate until the benzene is removed. Remove the air condenser, and boil until the solution foams. If any odor of hydrocarbons remains, add alcohol and boil down again. All the high-boiling hydrocarbons must be removed now, or the oil determinations will be high and erratic.

Dissolve the soap in 10 ml. of water. Add several drops of methyl red solution and 10 per cent hydrochloric acid from a

medicine dropper or pipet until the cloud of fatty acids just begins to form. Add 10 to 20 ml. of ethyl ether and a more dilute solution of hydrochloric acid until the aqueous phase turns faintly pink. More indicator may have to be added to the aqueous phase in order to give a perceptible color. This is the most difficult and important part of the procedure: difficult, because the ether extracts the indicator from the aqueous phase; important, because all the fatty acids must be liberated without freeing any phthalic acid. Any other monobasic acids (benzoic, rosin, etc.) which are present will be freed and will be extracted along with the fatty acids if soluble in ether.

If the resin contains phenolic resin, the phenols will be extracted by the ether and interfere with the oil determination. Decant the ether into a 250-ml. beaker, add 10 ml. of ether to the contents of the flask, and transfer to a separatory funnel. Run off the aqueous solution into the flask and the ether into the beaker. Extract once or twice more. Boil off the ether from the beaker on an electric hot plate. When only a few drops of water remain, place the beaker in an oven at 55° to 60° C. for several hours until the fatty acids are dry. Dissolve the dry fatty acids in 5 ml. of ether, and filter through a 3-cm. filter paper into a 30-ml. flask. Wash the fatty acids from the sides of the beaker with more ether, but keep the final volume of ether in the flask less than 20 ml. Evaporate the ether without boiling. Place the flask in the oven at 55° to 60° C. for several hours; then weigh at half-hour intervals until the weight is constant. Dissolve the fatty acids in 50 ml. of neutralized alcohol and titrate with aqueous 0.1 *N* potassium hydroxide to the phenolphthalein end point. Calculate the acid number of the fatty acids.

Duplicate titrations should agree within 5 units of acid number. If one is much lower than the other, the low one may have been heated too hot after the ether was removed and some anhydride formed. The acid number will be lowered by rosin, fossil-resin acids, or phenols and raised by benzoic acid.

From the amount of potassium hydroxide used, calculate the quantity which is added to the weight of the fatty acids to give the weight of the triglyceride. The weight of the triglyceride is called the weight of oil.

$$\text{Weight of fatty acid} + (0.00127) \times (\text{ml. of } 0.1 \text{ } N \text{ KOH}) = \text{weight of oil}$$

This calculation does not indicate that oil was put into the resin as such; it may have been all fatty acids.

A rosin test should be made on the extracted fatty acids rather than on the resin. Some fossil resins give color reaction very similar to rosin.

Phthalic Anhydride

To the aqueous solution remaining in the flask after the fatty acids have been extracted, add several milliliters of concentrated hydrochloric acid. Extract the solution three times with 10-ml. portions of ether, combine the ether extract in a 250-ml. beaker, and evaporate the ether. A few drops of water will remain with the phthalic acid.

In the meanwhile evaporate the aqueous solution until potassium chloride begins to crystallize out. Cool, add just enough water to dissolve the potassium chloride, and extract with ether three times as was done before. Add the ether extracts to the beaker which contains the phthalic acid, evaporate the ether, and place the beaker in a warm place (not over 50° C.) until the water and hydrochloric acid are removed.

Add 50 ml. of water and a few drops of phenolphthalein solution to the beaker. Run in from a buret a slight excess of 0.1 *N* potassium hydroxide. Heat until all the phthalic acid has dissolved, and titrate the hot solution with 0.1 *N* hydrochloric acid until the pink color barely disappears. The potassium hydroxide and hydrochloric acid solutions should be standardized with phthalic acid, phthalic anhydride, or potassium acid phthalate under the same conditions.

1 ml. of 0.1 *N* KOH = 0.0074 gram of phthalic anhydride

$f \times \text{phthalic anhydride} = \text{glyceryl phthalate}$

If the acid number of the resin was below 10 or if the theoretical amount of glycerol or more was used in the manufacture of the resin, the factor $f = 1.293$ can be used. If the acid number was higher than 10 or if the resin was made with a deficiency of glycerol, as is the practice in some plants, the factor is

$f = 1.293 - 0.0387 (\text{acid number})/\%$ of phthalic anhydride

The factor f is derived as follows: Assume that the acidity is due entirely to phthalic anhydride, and

$x = \text{phthalic anhydride present as glyceryl phthalate}$

$y = \text{phthalic anhydride to which the acidity is due}$

$a = x + y = \text{total phthalic anhydride}$

$b = \text{acid number of solids}$

$B = b \times (\text{weight of resin})$

Glyceryl phthalate = $y + 1.293 x = 0.001318 B + 1.293 (a - 0.001318 B)$

$f = \text{glyceryl phthalate}/a = \frac{1.293 a - 0.293 (0.001318) B}{a}$

$f = 1.293 - 0.000387 B/a = 1.293 - \frac{0.0387 b}{\text{per cent phthalic anhydride}}$

Two examples are given in Table I to illustrate the method. The first is a long-oil resin with a high acid number. The second is a short-oil resin that contains about 30 per cent of combined rosin.

TABLE I. ANALYSIS OF ALKYD RESINS

	Long-Oil Resin, High Acid No.		Short-Oil Resin, Low Acid No.	
Ash	Trace		Trace	
Solids, %	55.5		52.1	
Acid No.	27		6.8	
Sample, grams	1.5230	1.5125	1.2205	1.6521
Resin, gram	0.845	0.840	0.635	0.861
Fatty acids + resin acids, gram	0.6177	0.6140	0.4488	0.6093
0.1 <i>N</i> KOH to neutralize fatty acids, ml.	20.8	20.8	12.9	17.2
Acid No., fatty acids	192	190	163	164
Correction to convert fatty acids to triglyceride	0.0264	0.0264	0.0164	0.0218
Oil, gram	0.6441	0.6404	0.4652	0.6311
Oil, %	76.2	76.3	73.3	73.3
0.1 <i>N</i> KOH for phthalic anhydride, ml.	21.5	21.3	73.2	23.2
Phthalic anhydride, gram	0.1590	0.1575	0.127	0.172
Phthalic anhydride, %	18.80	18.75	20.0	20.0
f	1.237	1.237	1.280	1.280
Glyceryl phthalate, %	23.2	23.2	25.6	25.6
Oil + glyceryl phthalate, %	99.4	99.5	98.9	98.9

The per cent of oil plus glyceryl phthalate should be between 99 and 100. Occasionally check results give sums as low as 95. In these cases, the saponification numbers of the resins were sufficient to account for all the oil and phthalic anhydride found, which indicated either that an excess of glycerol was present or that part of the glycerol had been replaced by an alcohol with a higher combining weight. If the sum of oil plus glyceryl phthalate is too high, if the determinations for oil check each other, and if the saponification number accounts for all the fatty acid and phthalic anhydride found, the acid number of the phthalic acid should be determined, for it may be that some maleic anhydride was used in the resin.

RECEIVED April 11, 1936.

A Simplification of the Isohydric Indicator Method

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IN NORWAY most surface waters are acid, and in large parts of the country have an alkalinity (content of bicarbonates, humates, etc.) less than 0.0001 *N*. Waters with an alkalinity of about 0.00001 *N* and a pH value near 5 are common. Such waters are very corrosive of iron and concrete and many are lethal to trout and trout fry. Determination of pH has presented difficulties.

Acree and co-workers (1, 2, 3) have shown that large errors are possible when using the standard methods of pH determination in unbuffered solutions. They have also shown that the glass electrode and the isohydric indicator methods give satisfactory results, but these methods are not well suited for field work nor for laboratories doing only an occasional determination.

The author has developed a method which is essentially that of Acree and co-workers, but instead of having several indicator solutions previously neutralized to different pH, the neutralization is performed in two unequal volumes of the unknown fluid. The accuracy should be of the same order as with Acree's method, and the precision with a suitable ratio between the volumes seems adequate.

Modification of Isohydric Method

The method is based upon the fact that if identical volumes of an indicator solution, neutralized to a pH in the neighborhood of the acid (or alkaline) border of its useful range, are added to a small and to a large volume of an unknown fluid with a pH within the same range, the small volume will have a more acid (or alkaline) color than the large volume. If an indicator solution of the same pH as the fluid is used, the color in the volumes will be equal.

The easiest way to make the determination is to take two Nessler cylinders of the same size and measure out the identical indicator volumes and then the unequal fluid volumes. Titrate until the colors are the same, when looking down along the axis of the tubes; at this point the original pH is reached and the color may be compared with standards. Instead of microburets, dropping pipets may be used for field work, adding equal numbers of drops to the tubes between comparisons. The titrating liquids may be 0.001 *N* to 0.0001 *N* depending on circumstances. Suitable volumes are 20 and 100 ml. The use of alkaline indicator solution and titration

with acid is preferable, because absorption of carbon dioxide from the air may otherwise introduce errors. To avoid this, it is best to make a preliminary determination first, and in a second test add almost the total amounts of titrating liquid at once, using the greatest possible precision in the final titration.

The method has great elasticity. The two volumes need not be known, and the amount of indicator need not be known in relation to the volumes of fluids, except when compared with permanent standards. The concentration of the titrating liquid needs to be only approximately known. The essen-

tial features are that the added volumes of indicator solution be strictly equal, that the added amounts of titrating liquid before comparisons be equal, and that loss or absorption of carbon dioxide be prevented.

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RECEIVED March 11, 1936.

Sensitiveness of Magnesium Uranyl Acetate Reagent to Sodium and Potassium

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IN THE course of work upon a system for the analysis of the alkali and alkaline earth groups a study was made of the sensitiveness of magnesium uranyl acetate reagent to sodium and potassium. Since such data do not appear to be available for different dilutions of the reagent, in spite of the numerous papers upon the analytical applications of the reagent which have appeared, the results of the study may be of general interest.

Experimental

The reagent was prepared according to the directions of Noyes and Bray (1). Solutions of sodium and potassium nitrates containing 50 mg. per ml. of sodium and potassium were prepared from reagent chemicals and diluted as required. Redistilled 95 per cent alcohol was used.

The experiments were performed by mixing in small test tubes 1 ml. of sodium or potassium solution with a volume of reagent ranging from 0.1 to 2.0 ml. In some experiments 0.5 ml. of alcohol was added to the solution before mixing with the reagent. The results of the experiments in which 0.5 ml. of reagent was employed are presented in Table I.

TABLE I. TIME REQUIRED FOR PRECIPITATION
(1 ml. of solution mixed with 0.5 ml. of magnesium uranyl acetate reagent)

Sodium Mg.	Without Alcohol	With 0.5 Ml. of Alcohol	Potas- sium Mg.	Without Alcohol	With 0.5 Ml. of Alcohol
0.00	No ppt.	No ppt.	5	No ppt.	No ppt.
0.01	No ppt.	24 hr.	8	No ppt.	No ppt.
0.02	No ppt.	24 hr.	10	No ppt.	20 hr.
0.03	No ppt.	25-35 min.	12	2-50 min.
0.04	No ppt.	25-32 min.	14	No ppt.	1-5 min.
0.05	No ppt.	3-5 min.	15	22 min.
0.06	No ppt.	2 min.	16	3-4 hr.
0.12	No ppt.	18	8 min.
0.14	No ppt.	20	1-7 min.
0.16	3 hr.	25	<1 min.
0.18	5 min.-3 hr.
0.20	1 min.

The results of these and similar experiments in which other proportions of reagent to solution were employed are shown by Figure 1. Five minutes was taken as the observation time for this figure—that is, tests which failed to yield a precipitate within 5 minutes of mixing were regarded as negative. Tests which were positive within 5 minutes of mixing without the addition of alcohol are indicated by solid black circles, tests which failed to yield a precipitate without alcohol but which precipitated within the specified time when 0.5 ml. of alcohol was present are indicated by the half-shaded circles, while

tests which were negative even with the addition of alcohol are indicated by open circles. To avoid confusion, only those tests which were critical at any concentration of reagent have been plotted. The scales of Figure 1 are logarithmic to permit the inclusion of results for sodium and potassium in a single figure.

Discussion

It is evident from Figure 1 that the distinction between sodium and potassium is improved as the ratio of the volume of reagent to the volume of the solution tested is increased.

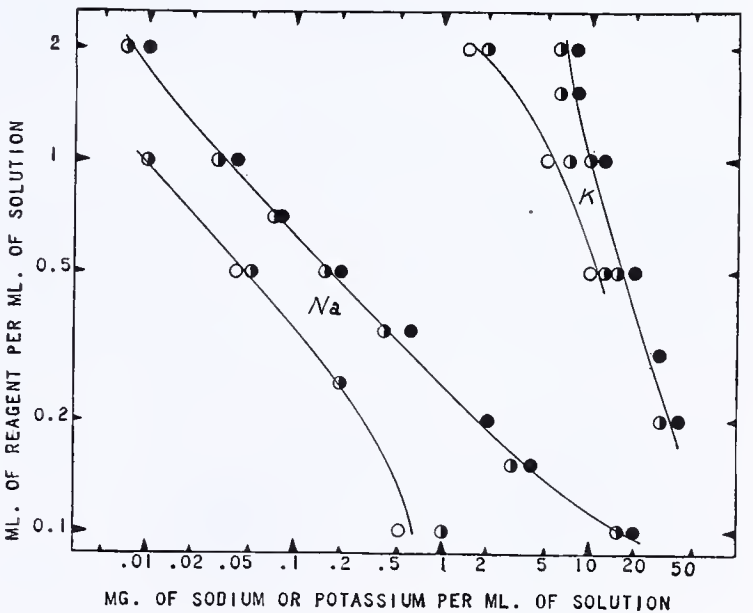


FIGURE 1. SENSITIVENESS OF MAGNESIUM URANYL ACETATE TO SODIUM AND POTASSIUM
(Volume of solution, 1.00 ml. Time, 5 minutes)

The addition of alcohol also increases the sensitivity of the reagent towards sodium more than towards potassium—a desirable result. With 2 ml. of the reagent to 1 ml. of the solution to be tested, however, the addition of 0.5 ml. of alcohol results in a slight turbidity which prevents the recognition of less than 0.01 mg. of sodium with certainty. This undoubtedly results from the fact that the reagent as prepared is saturated with the sodium compound. Unfortunately, it is not feasible to remove this sodium by including alcohol in the reagent, since uranyl ion is reduced by alcohol.

With 0.5 ml. of reagent and 0.5 ml. of alcohol per ml. of solution the presence of 10 mg. of potassium increases the sensitiveness of the test to sodium slightly; thus 0.02 mg. of sodium produces a precipitate under these conditions.

There is little danger of confusing potassium with sodium even if the quantity of potassium present slightly exceeds the amount permitted by the sensitivity of the test towards potassium. This arises from the fact that the potassium compound with the reagent crystallizes in long needles which may easily be distinguished from the granular precipitate of sodium magnesium uranyl acetate.

Summary

Data are presented showing how the sensitivity of magnesium uranyl acetate reagent towards sodium and potassium varies with the proportion of the reagent used in the test and with the presence of alcohol.

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RECEIVED June 2, 1936.

Check Valve for Wash Bottles

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THE check valve shown in Figure 1 has been found useful in wash bottles. With its use in delivery tube *G*, the water from the wash bottle neither spatters nor drips when pressure is applied or released. It also keeps the delivery tube full of water which may be siphoned from the wash bottle dropwise. This type of valve seats promptly and is held in position by the action of both pressure and gravity.

FOR ORGANIC SOLVENTS. The valve placed in tube *F*, through which the air enters the wash bottle, prevents the vapors of organic solvents from entering the mouth. This arrangement is most conveniently used with solvents such as ethyl and petroleum ethers, which do not condense in the valve chamber. For preventing back pressure, assembly *F* may be used in wash bottles containing either hot water or ammonia. The valves at *F* and *G* may be used separately or in combination.

Construction

Expand a small bulb 2 to 3 mm. larger than glass tubing which has an internal diameter of 4 mm. Thicken the walls of the tube at one side of the bulb to form the seat of the valve, as shown in *A*. Valve *B* is made from a glass rod with a diameter of 2.5 mm. Expand the end forming the valve by heating the upper tip of the rod (cut off squarely) while rotating it in a vertical position until

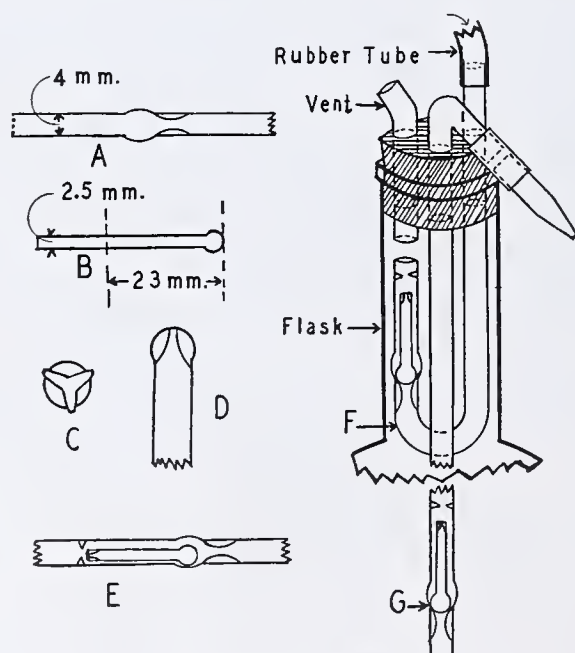


FIGURE 1. DIAGRAM

it will just pass into tube *A*. Grind with coarse and fine emery until a satisfactory seat is obtained. Cut valve rod *B* about 23 mm. long, heat the upper end, and press to the shape shown at *C* (end view) and *D* (side view) with a pair of tweezers to permit the air to pass readily. Insert the valve and, after heating tube *A* with a pointed flame, press in with a sharp pointed instrument to retain the valve as shown in *E*. Valve assembly *E* is bent to the shape shown at *F*, so that it will pass into the neck of the wash bottle, or it may be passed through the stopper and bent as in delivery tube *G*.

With valve *F* a vent tube is used which is closed with the thumb when the wash bottle is in use. To the upper part of tube *F* a piece of rubber tubing 25 to 30 cm. (10 to 12 inches) long is attached.

RECEIVED May 11, 1936.

Spectrographic Microdetermination of Zinc

IN AN ARTICLE entitled "Spectrographic Microdetermination of Zinc" [IND. ENG. CHEM., Anal. Ed., 8, 240 (1936)], the authors made the following statement: "Inasmuch as the concave grating spectrograph used by the authors is not so sensitive as the quartz prism instruments, the zinc present in the plant ash must be separated from the main constituents of the ash and concentrated before spectrographic methods can be applied."

It has been called to the authors' attention that this statement may be misinterpreted to reflect adversely upon the use of grating instruments for analytical work; thus they would like to point out that what was actually meant was that spectrographs of greater photographic speed exist than the grating spectrograph used, which make possible the arcking of a smaller amount of sample and hence possess greater absolute sensitivity.

On the other hand, the higher the resolution and dispersion of a spectrograph the slower the photographic speed, owing to the fact that the size of the diffracting medium is limited. These properties of high resolution and dispersion, however, tend to make for higher relative sensitivity, since the background is reduced by obtaining sharper lines and spacing them at greater distances. Thus the grating instrument employed is certainly on a par with all prism instruments as far as relative sensitivity is concerned, and in fact has been proved so by numerous experiments. Since for most work the size of the original sample is not the limiting factor, a high relative sensitivity is the most important attribute of the spectrograph for general analyses.

As a matter of fact, the sensitivity of the grating spectrograph used by the authors is sufficient for the positive detection of less than 0.001 mg. of zinc, all three of the persistent lines (3282.32, 3302.6, and 3345.0) being present when this amount of zinc is arcked.

ALBERT P. VANSELOW



INDUSTRIAL and ENGINEERING CHEMISTRY

Harrison E. Howe, Editor

Organic Reagents in Inorganic Analysis¹

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ALTHOUGH the methods of chemical analysis have been permanently influenced through the advances in all fields of chemistry, this influence is not always immediate, since in chemical analysis thorough testing and criticism are necessary and long periods of time frequently elapse before new methods and procedures become established. This is also true of the more recently popularized investigation and use of organic reagents. In inorganic analysis, which is undoubtedly one of the oldest branches of chemistry, inorganic reagents or purely inorganic reactions have, with a few exceptions, long dominated, even during a time when synthetic organic chemistry was experiencing striking triumphs through the evolution of classical syntheses and through the elucidation of constitution, etc., and an abundance of compounds was available. Up to the end of the preceding century only a few analysts devoted much consideration to organic reagents and then only where the value of such reagents was immediately obvious. As pioneers must be mentioned the French chemists, Denigès and Cazeneuve, with whose names are associated analytical reactions frequently used.

The genuine beginning of a systematic research into the possibilities of organic reagents, however, occurred at a later date. It was distinguished by the founding and development of the chemistry of the complex compounds by A. Werner and his school, further by the improvement of microchemical technic, and finally by the tendency toward rationalization and simplification of analytical methods. Today it is generally accepted that in the evaluation of analytical methods two criteria are determinative: the sensitivity and the specificity of the involved reactions. A comparison by both criteria of the effectiveness of inorganic and organic reagents shows that the latter exhibit many intrinsic advantages.

Although organic substances had been occasionally used earlier for precipitations and color reactions [the precipitation of metal oxalates, of hydroxides by organic bases, and the Griess reaction (60) for nitrous acid described in 1879, may be mentioned], it was only in 1905 that the significance of organic reagents in the analysis of inorganic substances was brought to attention in an obvious and emphatic manner. This was by the nickel reagent, diacetyldioxime (dimethylglyoxime), described by L. Tschugaeff, with which A. Brunck carried out a series of valuable separations. The Tschugaeff nickel reaction may still be considered as ideal in a certain sense. Because of the intense color and insolubility of the nickel salt, the reaction furnishes a sensitive method for the detection

of nickel; its exceptional purity and definite composition, making possible direct weighing, afford a direct determination of small amounts of nickel; and above all—and this is its particular merit—it is highly specific in its action. The nickel-diacetyldioxime reaction indicates for the first time, in that it hints at the great reservoir of organic compounds, the possibility of a far-reaching simplification of difficult analytical separations through the use of specifically acting organic reagents.

A survey of organic compounds for their use in solving analytical problems indicates that much empirical research is necessary, but that certain guideposts and directing principles are available for searching out new reagents or improving old reactions.

Salt-Forming Properties and Inner Complex Compounds

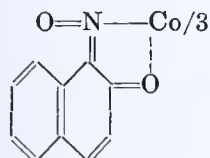
First consideration must be given to the salt-forming properties of the organic compound, which are due to the presence or the formation of definite acidic atomic groupings; such salt-forming groups are the sulfonic (SO_3H)—, sulfinic (SO_2H)—, carboxyl (COOH)—, hydroxyl (OH)—, sulfhydryl (SH)—, oxime (NOH)=, and imine (NH)= groups, the hydrogen atoms of which are replaceable by metal atoms. At the same time conditions must be such in the organic molecule that a complex compound can be formed through the saturation of the secondary valences of the metal atom contained as a neutral part in the molecule.

In the analytical evaluation of the salt-forming ability of an organic compound, as high a sensitivity and specificity as possible are first to be desired, assuming the salt to possess the necessary solubility relations (insolubility in water, solubility in organic reagents), and to have a color different from that of the reagent. Although one of the above acid-forming groups is indispensable for salt formation, other atoms or atomic groupings occurring in the molecule frequently exert essential influences on the specificity of the salt formation as well as on the color and the solubility of the salt concerned. It is important to observe that in all cases the metal not only replaces the acidic hydrogen atom but also is bound to other atoms of the same molecule through the saturation of the secondary valences of the metal atom (inner complex salt formation). The conditions affecting the dependence of analytical effects on constitution are therefore important because, as is well known, condensation and substitution reactions frequently cause great changes in the structure of organic molecules, thus modifying the salt-forming properties of the compounds, and this may be made profitable from an

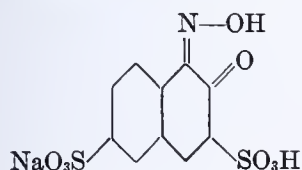
¹ Translation from the German by Harvey C. Diehl, University of Michigan.

tungsten, and vanadium, the procedures being useful analytically. However, a true salt of molybdenum or tungsten with benzoinoxime is not produced, but probably only addition compounds between molybdic or tungstic acid and benzoinoxime of the nature of the so-called heteropoly acids. Salicylaldoxime, which precipitates copper quantitatively in an acetic acid solution, also, according to Holzer (70), separates palladium, but not platinum, quantitatively from acid solution, the precipitate also being suitable for weighing. Both of the reagents mentioned therefore are not limited to one element in their activity. Such reagents are designated as specific reagents and are differentiated from the so-called special reagents—that is, those which are characteristic for a single substance. It should be noted that only a very few special reagents are available. However, in numerous cases through a choice of suitable experimental conditions a limitation of the activity of a specific reagent may result and the practical effects of a special reagent be achieved.

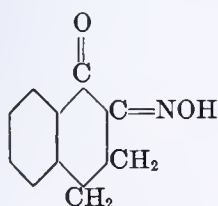
In a review of the specific activity of definite atomic groupings mention must be made of the cobalt reagent, α -nitroso- β -naphthol, described by Illinsky and von Knorre (71), which forms a reddish brown inner complex cobalt (III) salt



and which is one of the oldest organic precipitation reagents known. Also the isomeric β -nitroso- α -naphtholate of cobalt possesses an inner complex character which in color and solubility is inappreciably different from the compound first mentioned. Both cobalt nitroso compounds have, until recently, been used merely as precipitants, since the cobalt precipitates formed in acetic acid solutions do not have the theoretical composition. Recently Mayr and Feigl (88) have succeeded, by converting the cobalt into the trivalent state before precipitation, in obtaining a pure Co(III)-nitrosonaphtholate which after drying is suitable for weighing, and furnishes, therefore, a direct determination of cobalt. That the inner complex-forming groups are responsible for the cobalt affinity of both of the nitrosonaphthols is shown by nitroso R-salt,



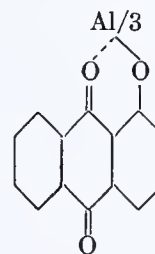
recommended by van Klooster (73) as a cobalt reagent, as well as the behavior of 2-isonitroso-1-ketotetralin



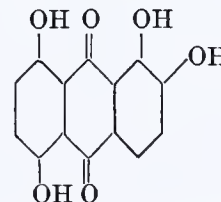
investigated by Strauss and Ekkard (113). The latter compound behaves toward cobalt salts in the same manner as the nitrosonaphtholates. Iron and palladium are also precipitated as inner complex salts by nitrosonaphthol and by this means may be separated from the similar elements aluminum and platinum. It is to be noted that in acid solution zirconium yields with the isomeric nitrosonaphthols insoluble zirconyl compounds, $(C_{10}H_6O_2N)_2(ZrO)$, of which that with the α -form is colored green-yellow, that with the β -form, red. The latter is recommended by Bellucci and Savoia (7) for the

sensitive detection of zirconium. A recent investigation by Mayr (87) has shown that α -nitro- β -naphthol may likewise be used for the separation and determination of cobalt. Undoubtedly this again involves the formation of an inner complex trivalent cobalt salt.

Insoluble inner complex salts, in which the organic component possesses the character of a dyestuff, as in the previously mentioned nitrosonaphtholates, are called color lakes. The color lakes of alizarin and other hydroxyanthraquinones possess considerable analytical significance. Atack (5) was the first to point out that aluminum could be detected with great sensitivity by means of the red color formed with alizarin-S (alizarin sulfonic acid). This is a question again of the formation of an inner complex salt corresponding to the coordination formula

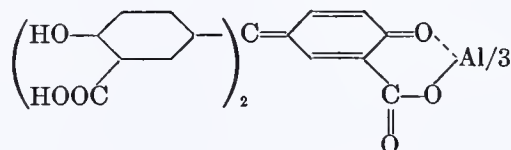


Atack, Underhill and Petermann (119), and Yoe and Hill (124) applied the alizarin reaction to the colorimetric determination of aluminum. Quinalizarin



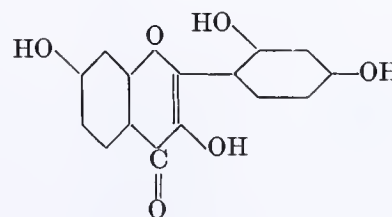
also forms lakes, and Fischer (50) has recommended the beryllium lake of quinalizarin for the detection and determination of beryllium. The magnesium lake of quinalizarin, according to Hahn (63), is suitable for the sensitive detection and for the colorimetric determination of magnesium.

Finally, there should be mentioned aurintricarboxylic acid, the yellow solution of which gives a red aluminum lake, probably corresponding to the coordination formula



Aurintricarboxylic acid was recommended as an aluminum reagent by Hammett and Sottery (65) and was later used by Winter and co-workers (123) and by Roller (105) for the colorimetric determination of aluminum.

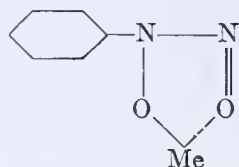
There should also be emphasized the lake which aluminum forms with the dyestuff of fustic wood, the so-called morin,



observed by Goppelsroeder (59). The reagent produces with aluminum salts in neutral or acetic acid solution an intense green fluorescence, which is due to a neutral aluminum salt of morin, $Al(C_{15}H_9O_7)_3$, in colloidal solution, and makes possible the recognition of 0.005 γ of aluminum (29, 108).

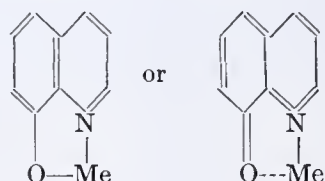
Although the morin reaction is the only fluorescent reaction of metals with organic compounds used analytically up to the present time, it is expected that still other examples will be found.

The ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N(NO)ONH_4$, recommended by Baudisch (6) in 1909 has been very widely used. This compound retains the name "cupferron," because it was first shown to be very suitable for the separation of copper and iron from numerous other metals. Here also, an inner complex salt is formed according to the formula



Later it was shown, especially by American investigators, that with control of the conditions of precipitation, a series of otherwise difficult separations of various metals can be effected and appreciably simplified. Thus the precipitation of thorium (116) and the separation of gallium (93) from Al, Cr, In, Ce, and U, of uranium (69) from Al, Zn, Ca, and Mg, of bismuth (96) from As and Sb, of tin (54, 95) from Co, Ni, Zn, Mn, As, Pb, and Sb, and finally the separation of zirconium (15) from Al have all been made possible by cupferron. In all these reactions there are again formed inner complex salts with the metal ion precipitated. These compounds are suitable forms in which to precipitate the metal, but are not satisfactory for weighing because the metallic compound is always contaminated with some of the reagent which is insoluble in water. The solubility in water (or in ammonia, alkalis, or acids) plays an important role in the practical use of organic reagents, especially for quantitative purposes. When an alcoholic or acetone solution of an organic reagent is added to an aqueous solution the problem is always complicated by the danger that the reagent will be thrown out as such by the water, thus contaminating the precipitate, from which it can be removed only with difficulty. In such cases the conversion of the precipitate into a form suitable for weighing, through ignition or other treatment, is necessary; the essential advantage of a low percentage of the determined material in the weighed precipitate is, however, then lost.

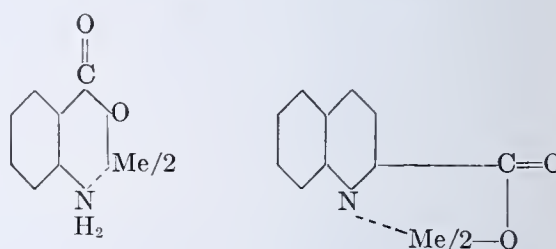
An example of an organic reagent forming inner complex compounds which have a satisfactory solubility and the theoretical composition is 8-hydroxyquinoline. This compound, which goes under the commercial name of "oxine," was introduced into analytical practice by F. L. Hahn (1926) and by R. Berg (1927). Oxine is very soluble in alcohol and acetic acid and with numerous metals yields insoluble, for the most part brightly colored, inner complex salts corresponding to the coordination formula



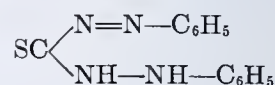
The metal salts of oxine as a rule may be dried at 105° to 140° C. and weighed. The phenolic nature of the reagent, moreover, makes possible a volumetric and a colorimetric determination, the former through bromination of the oxine with the formation of 5,7-dibromo-8-hydroxyquinoline, the latter through the color reaction with phosphotungstomolybdic acid, according to Folin and Denis (52), or through the coupling of the oxine with diazo compounds in alkaline solution. These volumetric and colorimetric determinations may be carried out either on the solution of the purified oxinate in acid or on the excess of reagent. With

oxine, too, the formation of inner complex salts depends on the atomic groupings as set forth in the coordination rules already given; accordingly the halogen derivatives of hydroxyquinoline such as 5,7-dichloro- and 5,7-dibromohydroxyquinoline are suitable for analytical purposes and even present certain advantages over the parent compound. Although hydroxyquinoline reacts with numerous metals, the reagent can be utilized in the solution of numerous problems in gravimetric analysis if control is exercised over the conditions of precipitation (8).

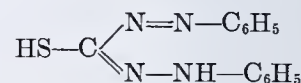
Two *o*-aminocarboxylic acids able to form inner complex compounds, which have been adapted recently to the purposes of gravimetric analysis, are anthranilic and quinaldinic acids. By means of anthranilic acid Funk (53) and co-workers have carried out a series of gravimetric determinations of divalent metals and have shown that through the bromometric determination of anthranilic acid a volumetric determination of the metal is possible. Quinaldinic acid was used by Rây and Bose (99) for the gravimetric determination of copper, cadmium, and zinc. In the analytical use of anthranilic and quinaldinic acids inner complex salts are formed according to the formulas



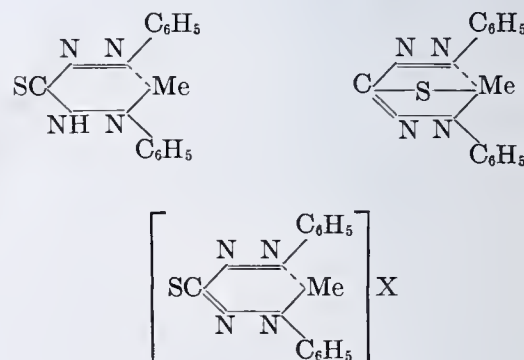
Of organic reagents in which a sulfur atom is involved in the formation of inner complex compounds, there should first be mentioned dithizone, thionalide, and rubeanic acid. Dithizone is the commercial name of a compound easily obtained, diphenylthiocarbazone,



investigated by Fischer (51), which reacts with numerous metals partly in the keto form as written, partly in the enol form



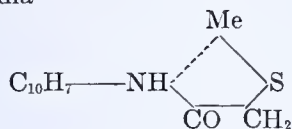
Derived from either the keto or the enol form, inner complex salts result corresponding to the coordination formulas



The first, produced in acid or neutral solution, is completely insoluble in water, although easily soluble in organic solvents, yielding intensely colored solutions; the latter form is preferred for univalent metals, and is equally insoluble in water but also insoluble in organic solvents. In spite of the lack of specificity in its action, by standardization of the

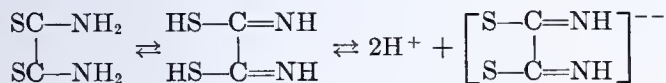
reaction conditions, dithizone furnishes numerous sensitive and important tests and colorimetric quantitative procedures.

Thionalide is the commercial name of thioglycollic acid β -aminonaphthalide, $\text{HS}\cdot\text{CH}_2\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, recommended by Berg and Roebling (10) as an analytical reagent. It is capable of forming inner complex salts corresponding to the coordination formula

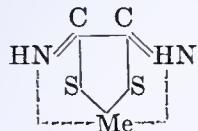


In neutral solutions thionalide reacts as a derivative of hydrogen sulfide with all heavy metals which are precipitated by the sulfide ion. Noteworthy is the precipitation of metal ions from mineral acid solution; all metal ions up to Cd(II) and Pb(II) are separated in the form of yellow or white precipitates. Although the depth of color of the heavy metal sulfides is not carried over in spite of the sulfur linkage, the sensitivity of the reaction is far greater than that of the sulfide precipitation. For example, in 5 ml. of solution arsenic can be identified in a dilution of 1 to 100,000,000 by the formation of a white precipitate. With thionalide also much of the difficulty due to its lack of specificity may be overcome by control of the conditions of precipitation—for example, by precipitating from mineral acid solution, or from alkaline solutions containing tartrate or cyanide. Of particular value is the reaction with thallium in alkaline solutions containing tartrate or cyanide, which is very specific and sensitive to a dilution of 1 to 10,000,000.

Thionalide also affords certain quantitative determinations. The copper and mercury salts may be isolated as such and after drying at 105° are suitable for weighing; moreover, the organic component of the precipitate may be determined iodometrically after removal of the excess reagent and the metal content calculated accordingly. Thioglycollic acid, the parent compound of thionalide, has been recommended by Lyons (85) for the colorimetric determination of small amounts of iron; it also shows the property characteristic of thionalide of forming insoluble inner complex salts. The effect of the amino group introduced into the series thioglycollic acid—thioglycollic acid analide—thioglycollic acid— β -aminonaphthalide is shown by the increasing insolubility of the metal salts (9). Rubeanic acid has recently been recommended by Rây and Rây (100, 101) as a qualitative reagent for copper, cobalt, and nickel. This compound, which is the diamide of dithioxalic acid, exists in solution in equilibrium with its tautomeric (aci), diimido, form, according to



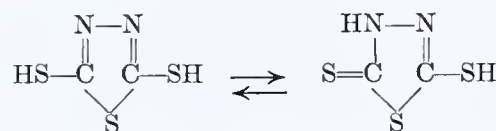
The acid form yields colored insoluble nickel, cobalt, and copper salts corresponding to inner complex compounds of the formula



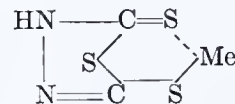
These complex salts are produced when the concentration of the aci form of the rubeanic acid is so great that the solubility product of the rubeanate formed is exceeded; as is seen from the above equation, this occurs when the hydrogen-ion concentration is diminished by the addition of sodium acetate, ammonium acetate, or alkalis. The copper, nickel, and cobalt compounds, precipitated quantitatively from strongly ammoniacal solution, when once formed, are insoluble in dilute mineral acids; this is in harmony with the idea that these compounds are inner complex salts. The stability of

these salts is exceeded only by the stability of the corresponding cyanide complexes, as is shown by the facts that the rubeanates are soluble in potassium cyanide solutions and are not precipitated from solutions containing cyanide. The sensitivity of the detection of copper, nickel, and cobalt by means of rubeanic acid is very high; in the form of a spot reaction as little as 0.006γ of copper, 0.012γ of nickel, and 0.03γ of cobalt can be detected. In a mixture of these three metals, the identification is still possible by means of a capillary separation procedure and in this manner 0.05γ of copper can be recognized in the presence of 20,000 times as much nickel (43).

A compound, capable of forming inner complex salts of high sulfur content with heavy metals, is 2,5-dimercaptothiodiazol, discovered by Dubsy and co-workers (20). This compound, functioning according to the tautomeric equilibrium



reacts in the mercapto form with numerous metals, forming inner complex salts of the following form:



Of particular interest is the color of the bismuth salt, which is deep red in contrast to the colors of other metal salts which are white to yellow. Here again the specificity caused by the difference in color is based on the formation of an inner complex ring as pictured above, and it is independent of the groups which can be easily introduced in place of the imino hydrogen atom.

Specificity in Normal Salts

So far only those reagents have been mentioned which, because of the neighboring position of the salt-forming and coordinating groups, have offered the possibility of forming the so-called inner complex salts. As pointed out, such inner complex compounds are frequently characterized by an abnormal solubility and by a deep coloration. These two properties frequently contribute a high sensitivity to methods for the detection and determination of metals but, on the other hand, at times leave something to be desired with respect to specificity. This is readily understood, inasmuch as the ability of nitrogen, oxygen, and sulfur atoms to coordinate in the formation of inner complex salts is not specific in action but is exerted toward numerous metal atoms, as is shown by numerous examples in that great class of substances, the amines and aquo compounds.

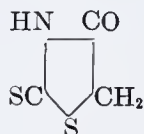
In attempting to arrive at a state in which the greatest possible number of specific reagents is available, those organic compounds which are merely capable of forming normal heteropolar salts should also be investigated for their analytical applications. Actually such compounds are frequently highly specific in their activity. Thus it has long been known that arsenic acid precipitated white insoluble zirconium arsenate from zirconium salts in solutions strongly acid with nitric or hydrochloric acids. Rice, Fogg, and James (103) were the first to find that this property of arsenic acid was also characteristic of organic derivatives of arsenic acid—for example, phenylarsonic acid. This acid makes possible the determination of zirconium and its separation from titanium and calcium. Thorium, which is very similar to zirconium, is precipitated by phenylarsonic acid only in solutions

buffered with acetate; this makes possible the determination of zirconium and thorium in the presence of each other by the same reagent. That the $-\text{AsO}(\text{OH})_2$ group alone is responsible for the activity of the organic derivatives of arsenic acid has been proved by Arnold and Chandlee (3) who showed that *n*-propylarsonic acid was equally satisfactory as a reagent for the quantitative estimation of zirconium. It should be noted that *p*-*n*-butylphenylarsonic acid also precipitates iron quantitatively (17).

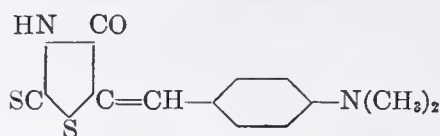
Phenylarsonic acid, in which substitutions have been made in various positions and in various manners, has been shown by Feigl and his co-workers to function just as the parent compound (27, 46). This made possible the introduction of a group which contributed color to the molecule with subsequent improvement in the sensitivity of the reaction. An example of this is *p*-dimethylbenzeneazophenylarsonic acid (27, 46) by means of which 0.1 γ of zirconium can be detected by a spot reaction. Further examples of the specific activity of more simply built organic compounds are indicated by the salt-forming properties of sulfinic acid, RSO_2H , and the analogous seleninic acid, RSeO_2H . It has been long known (115) that benzenesulfinic acid and ferric salts in mineral acid solutions yield a difficultly soluble, orange-yellow precipitate of the formula $\text{Fe}(\text{O}_2\text{SC}_6\text{H}_5)_3$. Other aromatic sulfinic acids behave in a similar manner, substitution in the aromatic nucleus having no effect. The analogous aromatic seleninic acids, according to Feigl and Anger (38), also form insoluble yellow ferric salts. This same work has also shown that tin (IV), ceric (IV), thorium (IV), and uranium (IV) salts are precipitated in strongly acid solutions by sulfinic and seleninic acids. The sulfinic and seleninic acids, therefore, exhibit a noteworthy specificity in action and this activity is again localized in particular groups. In contrast to the arsonic acids mentioned previously, in which it was irrelevant whether the arsonic group was coupled with aromatic or aliphatic residues, a direct combination of the sulfinic or seleninic groups with an aromatic ring is necessary (38). Of the compounds $\text{C}_6\text{H}_5\text{SO}_2\text{H}$, $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{H}$, and $\text{C}_6\text{H}_{11}\text{SO}_2\text{H}$, only the first has the power of precipitating the above metal ions from acid solution.

According to experiments to be reported later, it seems possible to use sulfinic acid for the quantitative macro- and microdetermination of the metals mentioned above (as well as for molybdenum and tungsten) and for their separation from other metals.

A further example of the specific action of certain atomic groupings in which no complex formation is involved is the heterocyclic compound rhodanine

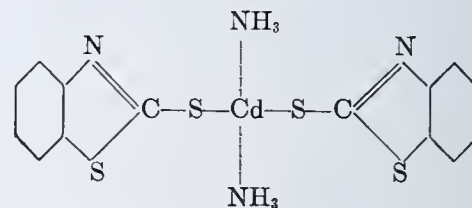


and its derivatives, which were investigated by Feigl (30). The imino hydrogen atom of rhodanine is replaceable by silver, mercury, gold, and palladium, producing a precipitate of yellow metal rhodanine compounds in acid solution. Because of the reactivity of the hydrogen atoms of the CH_2 group in the rhodanine molecule, condensation with numerous aldehydes and ketones is possible and all the derivatives so obtained have the same properties as the parent compound with respect to its precipitating ability. Thus, by the introduction of a chromophore group, colored silver salts can be obtained. Such a reagent is *p*-dimethylaminobenzalrhodanine



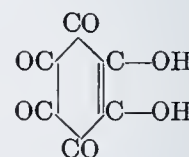
the violet silver salt of which permits the identification of silver in a dilution of 1 to 5,000,000, the most sensitive method known for silver up to the present time (36). *p*-Dimethylaminobenzalrhodanine has the advantage of yielding an insoluble silver salt but the disadvantage that the reagent must be used in alcohol or acetone solution. Accordingly the reagent is excellent for qualitative purposes but is not usable for gravimetric determinations, because the reagent is thrown down by water and cannot be quantitatively removed from the precipitate of silver salt. A survey of the possibilities of improving the reagent shows, however, that rhodanine also condenses with sulfonated aldehydes—for example, with *o*-benzaldehydesulfonic acid yielding a sulfonated benzalrhodanine which is readily soluble in water, alkalis, and acids (38).

Among the organic heavy metal compounds which do not belong to the group of inner complex compounds must be mentioned the cadmium salt of mercaptobenzothiazole

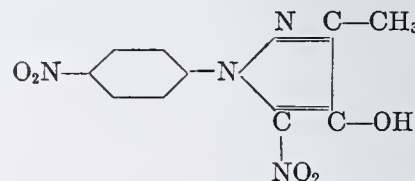


According to Spacu and Kuraš (112) this compound is produced by precipitation from an ammoniacal cadmium solution with mercaptobenzothiazole in the form of a yellow precipitate which is sufficiently pure to permit direct weighing in gravimetric work. The reagent is of particular value for the separation of cadmium from copper, since copper is precipitated in acid solution, cadmium being determined quantitatively in the filtrate from the copper precipitate.

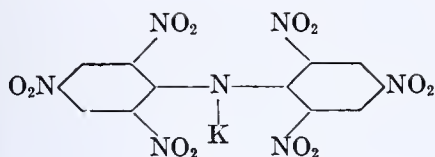
Even among the alkali and alkaline earth metals the formation of normal salts may make possible a differentiation of similar metals, as shown by the following examples. By means of rhodizonic acid



barium and strontium may be detected in the presence of magnesium and the alkali metals according to Feigl (25), and by maintaining certain experimental conditions barium may also be identified in the presence of calcium and strontium, and strontium in the presence of barium and calcium. A satisfactory reagent for gravimetric analysis has been found in picrolonic acid



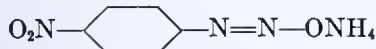
which forms insoluble salts of high molecular weight and of definite composition; the reagent was first recommended by Kissler (72) for the microchemical identification of potassium and has since been used for the gravimetric estimation of potassium (120), calcium (2, 21), lead (66), and thorium (67). According to Poluektoff (97) potassium can be identified by means of the water-soluble sodium salt of *p*-dipicrylamine, owing to the formation of an orange-yellow precipitate of the following formula:



This reaction is specific for potassium in the presence of the elements of groups 4 and 5, with the exception of rubidium and cesium, and only large amounts of ammonia must be previously removed. The identification of the NH_4 group is now possible by direct salt formation. This is by means of the sensitive reaction proposed by Riegler (104) involving *p*-nitrodiazobenzene



and alkali yielding the red ammonium salt of *p*-nitrophenyl-nitrosamine

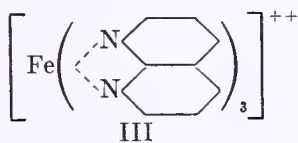
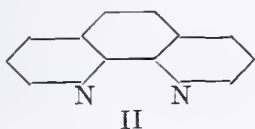
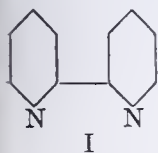


Only slightly investigated from an analytical viewpoint up to the present time are the reactions of complex metallic acids with organic bases. A few examples will indicate that this field is capable of expansion: $(\text{BiI}_4)^-$ is precipitated by cinchonine (84) and oxine (11), $[\text{Cd}(\text{CNS})_4]^{--}$ is precipitated by pyridine (107), and cadmium can be determined volumetrically by means of β -naphthoquinoline (11). Recently Krumholz and Krumholz (80) discovered a specific and sensitive test for zinc in the reaction of a basic styryl dye with $[\text{Zn}(\text{CNS})_4]^{--}$.

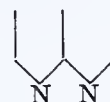
Finally it must be pointed out that normal salt formation with organic compounds plays an important role in the identification and estimation of anions. Well known are the gravimetric and volumetric methods for the determination of sulfate and tungstate by means of the organic base benzidine (74, 94) and of nitrate by the base nitron (16). The latter has recently been applied by Geilmann and Voigt (56) to the gravimetric determination of perhenate. The salt formation with methylene blue is the basis of the best macro- and microdetermination of perchlorate (14), and Allen and Furman (1) have recently recommended triphenyl tin chloride, $(\text{C}_6\text{H}_5)_3\text{SnCl}$, for the gravimetric determination of fluorine, the insoluble fluoride having the nature of a normal salt.

Neutral Constituents in Complex Salts and Adsorption Compounds

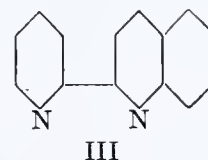
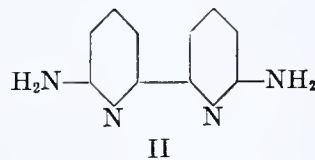
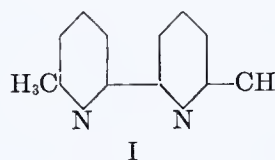
All the organic reagents mentioned previously, because of their acidic character or the additional presence of groups possessing residual valence, have had the power of forming normal salts or inner complex salts. Experience shows, however, there are many compounds of useful nature which do not possess hydrogen atoms replaceable by metals, but which, by means of secondary valence forces alone are able to form addition products with inorganic compounds. This addition to the metal of one or more molecules of the organic reagent as a "neutral constituent" may produce insoluble or characteristically colored complex compounds. Of this type of reaction we have all too few examples. Thus, α, α' -dipyridyl (I) and α, α' -phenanthroline (II) were found by Blau (13) to yield with ferrous salts the



intense red, water-soluble complex ion (III) which is stable toward dilute acids. This complex belongs to the hexamine type, since the six coordination positions of the iron atom are occupied by the nitrogen atoms of the three molecules of the organic base. Of especial interest is the great sensitivity and stability of the ferrous dipyrldyl and ferrous phenanthroline reactions, by means of which it is possible to detect even traces of ferrous salts (and therefore ferric by reduction). The reactions have been made the basis of a very sensitive colorimetric determination of iron by Feigl and Hamburg (42) but the procedure is difficult to carry out. In both reagents the activity is due to the presence of the group



but the activity of this group is appreciably influenced by substitution in the aromatic ring, as is shown by the examples, 6,6'-dimethyl-2,2'-dipyridyl (I), 6,6'-diamino-2,2'-dipyridyl (II), and 2(2-pyridyl)-quinoline (III).

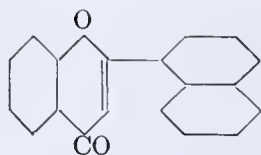


In spite of the apparently minor substitution, these compounds are incapable of forming the red ferrous complex. It should be observed that α, α' -dipyridyl and α, α' -phenanthroline also form addition compounds with other metals, although in acid solution a color reaction occurs only with iron and to a slight extent with copper, cobalt, and nickel ions. A great excess of reagent should be added, if necessary, in the identification or determination of iron in the presence of the metals mentioned.

A very characteristic example of the activity of an organic reagent as a neutral constituent is given by the well-known potassium xanthate reaction for molybdenum, investigated by Malowan (86) and by Koppel (79). There is produced the compound $\text{MoO}_3[\text{SC}(\text{SH})(\text{OC}_2\text{H}_5)_2]_2$ in which the xanthic acid functions as a neutral constituent. The activity here is associated with a definite atomic grouping, for it has been shown that other xanthates react in the same manner as ethyl xanthate. The activity of benzoinoxime toward molybdates and tungstates, which are precipitated in acid solution, as mentioned earlier, appears to involve the addition of benzoinoxime to molybdic or tungstic acids.

There should finally be listed the identification of sodium as sodium zinc uranyl acetate (77), in which it is assumed that the cause of the insolubility is the high molecular weight of the compound $[\text{NaZn}(\text{UO}_2)_3](\text{CH}_3\text{COO})_9 \cdot 9\text{H}_2\text{O}$.

In all the complex compounds previously mentioned there has always been a stoichiometric relation between the organic component and the metal atom involved. Combinations of organic components by auxiliary valences in nonstoichiometric ratios, such as the so-called adsorption compounds, are also of importance in analytical chemistry. The oldest known is the iodine-starch reaction, which is used for the identification of iodine and of oxidizing substances and has numerous applications in volumetric analysis. Similar to the starch reaction is the colored adsorption compound formed by the action of iodine or bromine on α -naphthoflavone (102).



The coloration of magnesium hydroxide by various dyes or alkaline solutions of dyes, which is used analytically, is again probably an adsorption phenomenon; probably salt formation with the dye occurs on the free surface of the magnesium hydroxide, as all the dyes found to be suitable are acidic in character. Recommended for the identification of small amounts of magnesium are alkaline solutions of the dyes quinalizarin (64), titan yellow (76), and *p*-nitrobenzeneazo- α -naphthol (27). There should also be mentioned in this connection the convenient differentiation of magnesite from dolomite described by Feigl (35), based on the coloration of magnesite by diphenylcarbazine. The phenomena associated with the coloration of crystalline and gelatinous precipitates have not yet been adequately investigated, although it is assumed that a series of specific colorations may be found for use in analytical chemistry.

Adsorption compounds between inorganic and organic substances are also applicable to quantitative analysis. Thus, Moser (92) has shown that Fe, Al, Cr, Sn, Zr, Ti, and Th are precipitated in acetic acid solutions by tannin; and that tungsten is quantitatively precipitated from a sulfuric acid solution of a tungstate by tannin. Apparently the precipitation involves the formation of adsorption compounds between tannin and the hydrolysis products of the metal salts. The adsorption compounds formed by certain organic dyes have found important application in volumetric analysis as adsorption indicators which have proved of excellent utility in the determination of end points, an application discovered by K. Fajans and later investigated by numerous other workers (78).

Organic Synthesis Involving the Substance to Be Determined

Fundamentally different in principle from all the examples previously considered for use as analytical reagents is the procedure in which the substance to be identified or determined is converted by synthesis into characteristic organic compounds. This conversion may be carried out in various ways. First, it may be accomplished by the direct synthesis of an organic compound. An example of this is the well-known qualitative and quantitative method of Griess (60) for nitrous acid, in which sulfanilic acid is diazotized by the nitrous acid, and then coupled with α -naphthylamine with the production of color. The great variation possible in the amine and in the coupling component used indicates that the formation of the $-\text{N}=\text{N}-$ group is essential.

The identification and determination of hydrogen sulfide by the synthesis of methylene blue from *p*-aminodimethylaniline, hydrogen sulfide, and ferric chloride, according to Fischer (49), may also be cited. Further examples are the well-known fluorescein test for bromides, in which red tetrabromofluorescein (eosin) is formed (55), the identification of sulfurous acid by the decoloration of malachite green (121), and the sensitive detection of boric acid by means of hydroxyanthraquinones (44) in which an inner complex boric acid ester is formed. By means of the latter reaction, through the addition of a 0.01 per cent solution of quinalizarin in concentrated sulfuric acid to a drop of the unknown solution, as little as 0.06 γ of boron may be identified. Hydrazine may be detected by condensation with benzaldehyde or even better with salicylaldehyde forming insoluble aldazines (31), $\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{N}=\text{CH}-\text{C}_6\text{H}_5$, and the precipitate may be weighed directly, after purification. Hydroxylamine can be

converted to nickel diacetyldioxime by reaction with diacetylmonoxime and then with a nickel salt, and identified and estimated as such (48, 68). Hydroxylamine may also be converted to yellow copper salicylaldoxime by reaction with salicylaldehyde and copper acetate (31) and in this manner be identified and determined quantitatively even in the presence of hydrazine (32).

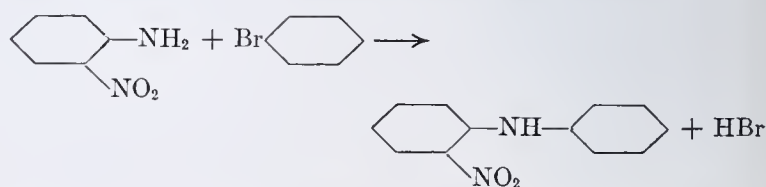
The activation of boric acid by polyvalent alcohols such as mannite, glycerol, etc., has been long known (12). The mannite- or glycerol-boric acid formed, in contrast to pure boric acid, acts as a monobasic acid of such strength that it liberates carbon dioxide from carbonates and may be titrated directly using phenolphthalein as indicator. This synthesis of boric acid complexes with polyvalent alcohols, the constitution of which has been investigated by J. Boeseken, may be used for the volumetric determination of boric acid (19, 57). Hahn (62) has recently worked out a very sensitive method of detecting traces of boric acid. An analogous intensification of acidity through combination with polyvalent alcohols also occurs with telluric (106) and germanic acids (118) and Poluektoff (98) has very recently shown that a volumetric determination of germanium is possible by this means.

Inorganic substances can also be employed indirectly in the synthesis of characteristic organic compounds, chiefly because of their oxidizing or reducing properties. Thus, by means of certain oxidizing agents colorless benzidine is easily converted into a blue merquinoid oxidation product



This change is produced by higher metal oxides, oxidizing and autoxidizing substances, and certain easily reduced complex compounds. By this means benzidine becomes a reagent for manganese (24, 33), cerium (26), lead (18), copper (47), thallium (24), phosphoric acid (34, 36, 37), cyanide (110), silicate (45), persulfate (89), and chromate (114). Similar to benzidine are 2,7-diaminofluorene (109) and tetramethyldiaminodiphenyl methane (117) which also form colored merquinoid compounds. According to unpublished experiments it is possible by color reactions to identify selenium by the oxidizing effect of selenium dioxide on organic compounds. Tin and vanadium may be identified by the reducing action of their lower valence states on cacotheline, a brucine derivative. This reaction, which was shown to be very sensitive by Gutzeit (61) and Ephraim (23), consists in a very characteristic color change from yellow to violet.

Finally, inorganic substances may be involved in organic syntheses because of their catalytic activity, or on the other hand inorganic reactions may be catalytically accelerated by organic materials. Such cases have been but seldom observed and described, but that it is possible in principle has been shown by Feigl and his co-workers. The reaction $2\text{NaN}_3 + \text{I}_2 = 2\text{NaI} + 3\text{N}_2$ is accelerated by carbon disulfide, involving the intermediate action of sodium azidodithiocarbonate; this makes possible not only the very sensitive detection of carbon disulfide but also a direct iodometric determination of azides (39). The acceleration of the reaction



by alkali iodides, first described by Goldberg (58), makes possible the specific identification of iodides (41). According

to unpublished experiments a very sensitive test for iodide and bromide seems possible by their catalytic effect on colored organic compounds.

Masking Reagents

As organic reagents should also be considered certain types of compounds the addition of which limits the activity of other reagents. As is well known, the concentration of a given ion in solution may be so diminished by the addition of substances which unite with the ion to form complex salts that an ion product sufficient to form a precipitate or cause a color reaction is no longer obtained. Thus we speak of the "masking" of a reaction, and call the reagent responsible for the disappearance of the ions necessary for the reaction, the "masking reagent." There are numerous organic compounds capable of acting as masking reagents. The precipitation of heavy metal ions as hydroxides is largely prevented by the alkali salts of hydroxy acids and by polyhydroxy compounds such as tartrate, citrate, glycerol, mannite, and various sugars. Occasionally the masking may be so complete that the formation of many inner complex salts may not occur—for example, precipitations with oxine or color reactions with thionalide.

Through deliberate selection of suitable masking reagents it has already been possible to secure wide applications for these reagents. Sulfosalicylic acid was recommended by Moser (90, 91) as a precise, fractional masking agent. The masking of certain reactions of mercury, copper, nickel, and cobalt by cyanide and thiocyanate has been known for a long time. The alkali salts of many organic acids are used as buffers for the regulation of hydrogen-ion concentration. A characteristic example in the analysis of anions is that suggested by Kurtenacker (81, 82, 83) in which sulfite is masked by the addition of formaldehyde, forming sulfoxylates which are stable toward iodine, making possible an excellent iodometric titration of thiosulfate in the presence of sulfite.

Of greater importance are organic compounds which can be used as protective colloids in the preparation of stable sols of insoluble metal salts for colorimetric purposes. For this purpose gelatin, egg albumin, dextrin, and gum arabic have long been used. Researches with V. Anger, which have not yet been completed, indicate that the water-soluble cellulose ethers are excellent and versatile peptizing agents. With the development and improvement of colorimetric methods by the use of the photoelectric cell, color reactions with organic reagents and the dispersion of insoluble compounds with the help of organic substances will doubtless receive increasing attention.

Finally, brief mention should be made of the use of organic liquids (principally alcohol and acetone) as solvents for certain reagents and as addition reagents to complete the precipitation of materials from aqueous solutions. Of great significance also are solvents immiscible with water, such as ether, amyl alcohol, carbon tetrachloride, etc., which can be used for the extraction of certain substances and their concentration into smaller volumes. The extraction of dithizonates by immiscible solvents has made possible the detection and determination of many heavy metal salts by the organic reagent dithizone. Furthermore, substances which are not soluble in organic liquids can sometimes be concentrated at the water-organic liquid interface by shaking with immiscible organic liquids and by this means rendered visible in small amounts.

Summary and Review

1. Organic reagents have an increasing analytical significance, since their use greatly increases the specificity and the sensitivity of analytical reactions, introducing a simplification and rationalization of analytical methods, particularly in microchemical analysis.

2. The reactions of inorganic substances with organic reagents can be divided into the following types: (a) formation of normal salts, (b) formation of inner complex salts, (c) formation of complex compounds with organic components as neutral constituents, (d) formation of adsorption compounds, (e) direct synthesis of organic compounds lacking the characteristics of salts, (f) participation as oxidizing or reducing agents in the synthesis of organic compounds, and (g) catalytic activity in the synthesis of organic compounds.

3. A methodical investigation of all the types of reactions gathered under (2) promises to yield new and valuable reagents. Few of the reactions considered up to the present time have been of types (a), (c), or (g), especially catalytic reactions and those reactions which yield fluorescent substances.

4. The effectiveness of the reagents of all the types gathered under (2) depends on the specific atomic groupings contained in the molecule. With a knowledge of the specific activity of definite groups it is possible to work systematically toward the improvement of the reagents.

5. Distinction must be made between specific reagents and special reagents. The former react in a definite manner toward various substances, while the latter are limited in activity to a single substance. Up to the present there are only a few good special reagents. For practical purposes, however, the activity of specific reagents can be adequately limited by the careful control of conditions, the use of masking reagents, etc., to make them widely applicable.

6. In view of the simplification of colorimetric methods and the improvement in accuracy of colorimetric measurements by means of the photoelectric colorimeter, an increasing significance must be attributed to the discovery of new color reactions and of peptizing agents for insoluble but colored precipitates.

7. Associated with the vast numbers of organic compounds available for use in analytical chemistry is the danger of an unnecessary increase in the number of organic reagents. In this work, therefore, only those reactions should be described which display significant improvements in sensitivity and specificity or have a bearing on the theory of specific affinity.

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RECEIVED September 8, 1936. This paper was prepared for the Analytical Edition upon special request to Dr. Feigl, professor at the University of Vienna, because of his extensive contributions to this subject.

Anticipating the demand which will arise for reprints of this article, the Mack Printing Company, Easton, Pa., will accept orders for reprints until January 1, 1937. Units of 50 copies can be supplied in the 6 x 9 size with covers for \$6.00. Single copies, 20 cents, postage paid. Bulk shipments will be made by express collect.

Problems in Analysis

FACTS which are ascertainable only through analysis of compounds and mixtures are basic to most of the work done in chemistry and chemical engineering. Research of a high order is carried on in analytical procedure in many laboratories. While the majority of such workers have a field of particular interest, there are nevertheless a number of men of ability, especially those directing the research of others, who would be glad to know of problems in analysis which would be of interest to industry and upon which they might like to work.

As a service both to industry and to these research analysts, we shall be pleased to receive and publish such problems. It should be understood that those who decide to work upon them will let us know, so that we in turn may help establish contacts between those interested in such research problems and those who would like to follow up the work in order to render possible assistance, and to be certain that some progress is made toward publishable results.

[EDITOR]

Analysis by "Internal" Electrolysis

I. Determination of Bismuth and Copper in Lead Alloys Containing Antimony and Tin

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ELECTROANALYSIS by the spontaneous discharge of a galvanic cell in which a solution of the alloy to be analyzed constitutes the catholyte, has been named "internal" electrolysis (8, 9), emphasizing the distinction from ordinary electroanalysis in which the e.m.f. is externally applied. The earliest reference to this method is by Ullgren (11), who plated small quantities of copper from sulfate solution by means of zinc-platinum, cadmium-platinum, and aluminum-platinum cells. Later work includes that of François (5), Hollard (6), Tutundzic (10), Sand (8), and Collin (1-4).

In view of the inherent advantages of "internal" electroanalysis, it is surprising that it has not been more widely used. This method is unique in that the cathode potential is automatically limited. Since platinum anodes are not employed, separations may be made in chloride solution in the absence of an anodic depolarizer. In "internal" electroanalysis iron does not interfere with the plating of metals from chloride or sulfate solution because the anodes are shielded. The method is rapid and is therefore suitable for routine analysis; the apparatus required is inexpensive.

The method is subject, however, to certain limitations and involves a number of experimental difficulties. In general, its application is limited to the determination of small quantities of metals. Thus it has its greatest usefulness in the separation of impurities from the bulk of the base metal, as of bismuth and copper from lead. Frequently the method serves only for a preliminary separation, other methods being more suitable for the final determination. There are also certain limitations imposed upon the choice of the anode metal which in turn limit its applicability: The cell will not function unless there is free and uninterrupted dissolution of the anode—i. e., the anode must not become passive in the anolyte. The value of the anode potential must be such as to cause rapid and complete deposition of the metal being determined.

Collin (1), working with Sand (8), proposed the lead-platinum cell for the determination of bismuth and copper in lead and lead-antimony alloys. The present authors have modified the Sand and Collin method and have extended its applicability to lead-tin alloys. Certain improvements in apparatus have been introduced. The chief differences between the authors' apparatus and method and those of Sand and Collin are as follows:

A new electrode assembly has been designed. Norton alundum shells (7) have been substituted for parchment paper as anode envelopes. In this laboratory parchment paper was found to stretch and become increasingly porous in hot nitric acid solution.

The bismuth-copper plate is weighed directly. After solution, the copper is titrated iodometrically and the bismuth calculated by difference. This obviates the unsatisfactory basic carbonate separation of bismuth and copper.

Silver is removed as iodide rather than chloride because of the lower solubility of silver iodide, a necessary measure when separating the small quantities of silver usually found in commercial lead. Another objection to chloride is that its presence contributes to the production of a bismuth plate physically unsuited to direct weighing.

The authors have shown that the method can be used in

nitric-hydrofluoric acid mixtures, thus extending its applicability to lead-tin alloys.

Apparatus

The apparatus is shown diagrammatically in Figure 1. It consists of two lead anodes enclosed in alundum shells (19 × 90 mm. RA No. 84 or RA No. 360, R. Norton and Co., 7) and a single platinum gauze cathode (2.5 cm. in diameter and 4 cm. in length), arranged to fit into a 400-ml. beaker. The three electrodes are connected to a single binding post so that good electrical contact is made. The electrode support is shown in detail in Figure 2.

The anodes are made by winding pure lead wire (2.5 mm. in diameter × 70 cm. in length) around glass tubing (5 mm. in diameter) in the form of a compact helix, leaving enough wire at the top to act as a lead to the binding post. The surface of the anode should in general be as large as is practically possible to ensure rapid plating.

A glass corkscrew stirrer with tungsten shaft is used to stir the catholyte. It is driven by a motor capable of 1000 r. p. m. and geared so that the solution is drawn in towards the cathode.

An anolyte reservoir is provided which permits the flushing out of the anode chambers during an electrolysis. In this way any platable metal ions which may find their way through the shells can be returned to the catholyte. Flushing of the anode chamber also tends to prevent anodic concentration polarization, although this effect proves to be negligible if the anode area is large.

THE ANODE SHELLS. The porosity of the alundum thimbles used as anode shells plays a very important role in the success of the method. When a shell of this composition (alumina with aluminum silicate as a binder) is subjected to treatment with hot nitric acid, a certain amount of hydrolysis of the aluminum silicate takes place. The gelatinous hydrolytic products tend to reduce the porosity of the shell. In an electrolysis the formation of such a precipitate in the anode shells will increase the internal resistance of the cell to such an extent that the cathodic plating will be prohibitively slow. Obviously, then, in devising a method in which an internal electrolytic separation is made from nitric acid solution, the procedure used must be such that hydrolysis of the material of the anode shells is avoided. Thus, in the method described below the temperature of the solution is not allowed to go above 75° C. The method further specifies that tartaric acid be added to the catholyte in all electrolyses, even though its presence is not required in the solution of the alloy.

Experience has shown that new alun-

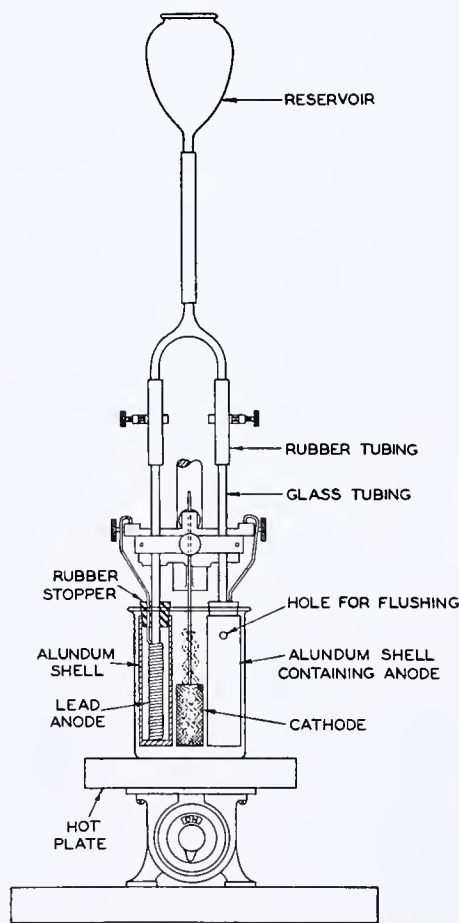


FIGURE 1. DIAGRAM OF APPARATUS

dum shells are nearly always easily clogged by hydrolysis. Continual use in any internal electrolysis will gradually wash out the hydrolyzed material to such an extent that quantitative plating from nitrate solution can be obtained. In order to accelerate the process of opening up new or contaminated shells a preliminary acid treatment has been devised (see below). Even after subjecting the shells to the vigorous "opening" treatment, however, the plating may be slow for the first three or four electrolyses.

If, during the electrolysis of a copper-bismuth solution, the shells become clogged, the addition of a little chloride will immediately open the shells up and permit rapid deposition of the metals.

The optimum temperature for plating from lead solutions containing chloride is 80° to 90° C., for at lower temperatures the internal resistance of the cell may be increased by the formation of lead chloride on the anodes or in the shell walls. The use of chloride in the solutions may make it necessary to dissolve and replate the deposit.

Despite the difficulties mentioned above the authors have found that alundum thimbles provide the most satisfactory means of shielding the anodes. Two types of shells have been tested: the dense RA No. 84 shells and the less dense RA No. 360 shells of R. Norton and Co. Both types are satisfactory for use in the electrolysis, provided they are open. The plates obtained (especially those which contain much bismuth) are better when the No. 84 shells are used because the plating is slower. On the other hand, the No. 360 shells are more easily opened and kept open, and the time of electrolysis is shorter.

CONDITIONING AND TESTING OF THE ANODE SHELLS. The following procedure is recommended for opening up or cleaning alundum anode shells:

1. Draw 400 ml. of hot concentrated hydrochloric acid through the shell into a flask by means of suction. Remove and reserve the solution.

2. Draw 400 ml. of hot nitric-tartaric acid solution (40 ml. of concentrated nitric acid plus 20 grams of tartaric acid dissolved in 360 ml. of water) through the shell.

3. Repeat the chloride wash of paragraph 1. Then draw warm distilled water through the shell to remove all chloride. (The chloride must be removed since its presence may invalidate the conclusions drawn from the testing of the shells by paragraph 4.)

4. Prepare a solution containing 8 ml. of nitric acid, 1 gram of tartaric acid, and 10.0 mg. of copper as copper nitrate in a volume of 150 ml. Boil to expel oxides of nitrogen. (If these fumes are not expelled the plate may be dark.) Dilute to 250-ml. volume. Cool to 65° C. Electrolyze at 65° to 75° C. as described below in Procedure A, paragraph 3, using as an anolyte a 3 per cent nitric acid solution. Weigh the plate and compare the result with the amount of copper added.

Once opened, the shells usually require no further treatment. To prevent an accumulation of salts in the walls, it is advisable to remove and wash the shells with distilled water after use.

The Method

The sample is dissolved in a mixture of either nitric and tartaric acids or nitric and hydrofluoric acids. Antimony and arsenic are oxidized to their higher valence states with permanganate. Silver is removed as iodide. Bismuth and copper are plated out with a lead-platinum couple and the combined deposit is weighed. The plate is then dissolved and the copper titrated iodometrically. Bismuth is calculated by difference.

Such elements as calcium, cadmium, and zinc do not interfere. Iron in amounts usually present in lead does not interfere. Antimony and arsenic do not interfere when present in the pentavalent form in nitric-tartaric or nitric-hydrofluoric acid solution. Quadrivalent tin does not interfere even when present in large quantities in nitric-hydrofluoric acid solution.

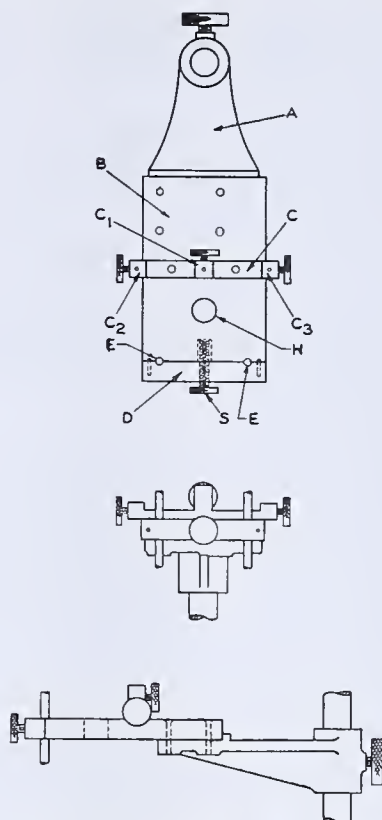


FIGURE 2. DETAIL OF ELECTRODE SUPPORT

- A. Cast-metal supporting arm
- B. Hard-rubber board
- C. Metal binding post (stainless steel or oxidized brass)
- C₁. Cathode support
- C₂, C₃. Anode supports
- D. Removable anode support
- E. Holes for glass tubes which support anodes
- H. Hole for stirrer
- S. Removable threaded screw

Selenium interferes with the determination, but preliminary experiments indicate that very small quantities of tellurium may be present, provided it is in the hexavalent form.

SIZE OF SAMPLE. The method is subject to certain limitations as regards the amount of bismuth that can be handled. Bismuth alone plates out in loose granular form. Under these conditions lead and other metal salts may be mechanically occluded in the plate, thus causing high results. When copper is plated with the bismuth, however, the deposit is much more compact and adherent; as much as 10 mg. of bismuth can be handled if the amount of copper present equals or exceeds that of the bismuth. If less copper than bismuth is present the plate may be contaminated and in such a deposit the occluded impurities—e. g. antimony, arsenic, iron, etc.—may cause an appreciable blank in the copper titration.

In order, then, to ensure correct results for both copper and bismuth in an analysis of a lead or lead-tin alloy which contains more bismuth than copper, the analyst must either dissolve the first plate and re-electrolyze from pure nitric acid-tartrate solution (using 3 per cent nitric acid solution as the anolyte), or add a known amount of copper to the solution of the alloy before electrolysis to make the bismuth-copper ratio less than unity. The latter procedure is preferable as requiring less time, and is therefore recommended in the method below.

SOLUTION OF THE SAMPLE. Alloys containing arsenic, antimony, or small amounts of tin are soluble in nitric acid-tartaric acid mixture. For larger amounts of tin the tartaric acid is replaced by hydrofluoric acid.

It is obviously desirable to use as little hydrofluoric acid as possible. On the other hand, the amount of this acid used must be sufficient to ensure solution of the tin during the vigorous boiling previous to electrolysis (see below). Procedure B is suitable for the analysis of alloys containing as much as 50 per cent of tin. With alloys containing less than 10 per cent of tin the amount of acid used can be reduced. Once the tin has precipitated, however, it is extremely difficult to redissolve it by adding more fluoride.

When tin is dissolved in nitric-hydrofluoric acid solution it tends to remain in the bivalent state unless nitrous acid is produced in the solution to ensure oxidation. When dealing with 50:50 lead-tin solders there is usually sufficient nitrous acid produced to catalyze the solution and oxidation of the tin. With alloys of low lead content it is advisable to add sodium nitrite.

STANDARDIZATION OF SODIUM THIOSULFATE SOLUTION. Prepare a standard copper nitrate solution containing 0.5 gram of copper per liter. Pipet a sample from this solution which will give approximately the same size thiosulfate titer as that given by the unknown sample. Transfer to a 250-ml. wide-mouthed flask. Add 1 ml. of (1 to 1) sulfuric acid. Take just to fumes of sulfur trioxide twice to expel all nitrates. Cool. Wash down the sides of the flask and add 25 ml. of water. Cool to room temperature.

Add 5 ml. of a freshly prepared 40 per cent solution of potassium iodide and mix well. Add 5 ml. of a clear, freshly prepared 20 per cent solution of sodium thiocyanate and titrate immediately with 0.025 *N* sodium thiosulfate. When the end point is approached add 5 ml. of clear 1 per cent starch solution and then complete the titration.

A. PROCEDURE FOR ALLOYS SOLUBLE IN NITRIC ACID-TARTARIC ACID SOLUTION. (This procedure is suitable as written for 1 per cent antimony-lead alloy containing less than 0.05 per cent of silver and 0.005 to 0.1 per cent of bismuth.)

1. Weigh out 10 grams of the sample and transfer to a 400-ml. beaker. Add 1 gram of tartaric acid and 80 ml. of nitric acid (20 per cent). Cover with a watch glass and heat gently until solution is complete. Boil for 1 minute to expel most of the nitrous acid fumes. Dilute to 150-ml. volume with cold water. Cool to 40° C. Add potassium permanganate (1 per cent solution) while stirring until the solution acquires a violet tint which lasts a minute or two. Let stand or heat gently to dispel the color.

2. (In case silver is known to be absent this paragraph can be omitted.) Add 2 ml. of potassium iodide (1 per cent solution) while stirring. Allow to stand 5 to 10 minutes at 35° to 40° C., avoiding direct sunlight. (If at any time during the precipitation or filtration of the silver iodide there is evidence that the potassium iodide is being oxidized, the solution can be decolorized by adding a drop or two of freshly prepared sulfurous acid solution.) Filter with suction through asbestos into a second 400-ml. beaker. Wash with water or with 3 per cent tartaric acid solution in the event that the antimony content of the alloy is high. Discard the precipitate. Dilute the filtrate to 250-ml. volume. Place 2 or 3 glass beads in the beaker. Cover and heat to boiling. Boil vigorously until the solution has become colorless and then for an additional 10 minutes.

3. Dilute the solution to 250 to 300 ml. (Standard copper nitrate solution should be added at this point if the ratio of bismuth to copper in the alloy is greater than unity.) Cool to 65° C. Add 0.2 to 0.3 gram of urea. Electrolyze with rapid stirring (800 to 1000 r. p. m.) at 65° to 75° C. with a lead-platinum couple. (Anolyte for the lead-platinum couple: a 3 per cent nitric acid solution containing 50 grams of pure lead nitrate per liter.) Flush out the anode chambers, wash down the sides of the beaker and anode shells, and add small amounts of urea, once or twice during the electrolysis. When the plating is completed (as indicated by failure to plate on new surface when level of solution is raised) wash away the acid-lead nitrate solution with approximately 1 liter of distilled water by siphoning. (If there is any reason to suspect that the plate contains other

metals besides copper and bismuth, proceed as follows: Dissolve the plate from the electrode in 8 ml. of nitric acid. Dilute to 150 ml. Boil to expel fumes. Dilute to 250 ml. Add 1 gram tartaric acid. Cool to 65° C. Electrolyze as described above using as anolyte a 3 per cent nitric acid solution.) Remove the beaker and rapidly replace with another containing distilled water. Detach the electrode, wash in alcohol and ether, and dry with an electric fan. Weigh.

4. Place the electrode in a 250-ml. wide-mouthed flask and dissolve the plate with 5 ml. of 3 per cent hydrogen peroxide and 1 ml. of 1 to 1 sulfuric acid. Wash the electrode well and remove. Take the solution to fumes of sulfur trioxide to destroy all traces of peroxide. Titrate the copper with thiosulfate as directed above under standardization of the latter solution. (In the titration of samples containing bismuth the starch solution must be added after the thiocyanate and before the beginning of the titration.)

B. PROCEDURE FOR ALLOYS SOLUBLE IN NITRIC-HYDROFLUORIC ACID SOLUTION. (This procedure is suitable as written for a 50 per cent tin-lead alloy containing less than 0.05 per cent of silver and 0.005 to 0.1 per cent of bismuth.)

1. Place 10 grams of the sample in a 600-ml. beaker containing 20 ml. of nitric acid, 15 ml. of hydrofluoric acid (48 per cent), and 100 ml. of distilled water. Cover and heat gently (water bath) until solution of the alloy is complete (caution). Boil for 1 minute to expel most of the nitrous acid fumes. Dilute to 300 ml. with cold water. Cool the solution to 40° C. Add 1 per cent potassium permanganate solution until the solution remains permanently colored or fades but very slowly.

2. (If silver is known to be absent omit this paragraph.) Add 2 ml. of 1 per cent potassium iodide. Just decolorize the solution by adding dropwise freshly prepared sulfurous acid solution. Digest cold for 5 to 10 minutes, avoiding direct sunlight. Decolorize again if necessary. Filter through asbestos. Wash with cold water. Discard precipitate. Dilute filtrate to 350 ml.

3. Drop 2 or 3 glass beads in the filtrate, cover, and heat to boiling. Boil vigorously until the solution is colorless and then for 5 to 10 minutes longer.

4. Dilute to 350- to 400-ml. volume. Color again with potassium permanganate. Add 2 grams of tartaric acid. Add standard copper nitrate solution if necessary. Proceed as in paragraph 3 of Procedure A.

TABLE I. DETERMINATION OF BISMUTH AND COPPER IN THE PRESENCE OF LEAD AND COMMON IMPURITIES OF LEAD

Lead Present	Copper Present	Bismuth Present	Copper and Bismuth Present	Bismuth Found
Grams	Mg.	Mg.	Mg.	Mg.
20	14.4	14.5	28.9	29.3
40	14.4	14.5	28.9	29.4
20	5.7	5.8	11.5	11.4
20	5.7	5.8	11.5	11.5
20	5.7	5.8	11.5	11.6
20	2.9	2.9	5.8	5.6
40	2.9	2.9	5.8	5.9

TABLE II. DETERMINATION OF BISMUTH AND COPPER IN THE PRESENCE OF LEAD AND COMMON IMPURITIES OF LEAD*

Lead Present	Copper Present	Copper Found	Bismuth Present	Bismuth Found	Copper and Bismuth Present	Copper and Bismuth Found
Grams	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
10	13.7	13.7	14.7	14.8	28.3	28.5
10	13.7	13.7	2.9	2.7	16.6	16.4
10	2.8	2.7	2.9	2.9	5.7	5.7
10	5.5	5.4	5.9	5.8	11.4	11.2
10	1.1	1.1	5.9	5.9	7.0	7.0
10	5.5	5.5	5.9	5.8	11.4	11.3
10	5.5	5.5	5.9	5.8	11.4	11.3
10	2.8	...	2.9	...	5.7	5.6
10	2.8	2.7	2.9	2.8	5.7	5.6
10	2.8	2.7	5.9	6.0	8.6	8.8
10	5.5	5.5	5.9	6.1	11.4	11.6

* No tin was added in these experiments.

TABLE III. DETERMINATION OF BISMUTH AND COPPER IN SYNTHETIC LEAD SOLUTIONS AFTER SEPARATION OF SILVER

Copper Present	Copper Found	Bismuth Present	Bismuth Found	Bismuth and Copper Present	Bismuth and Copper Found	Antimony Present	Silver Present
Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
11.0	10.7	5.0	5.1	16.0	15.8	100	5
4.4	4.2	5.0	5.0	9.4	9.2	100	1
4.4	4.3	5.0	5.1	9.4	9.4	...	5
4.4	4.4	2.5	2.5	6.9	6.9	50	1
4.4	4.2	5.0	5.2	9.4	9.4
4.4	4.3	5.0	5.2	9.4	9.5
4.4	4.4	1.0	1.1	5.4	5.5	100	5
11.0	10.9	10.0	10.4	21.0	21.3	100	5

Experimental

Synthetic solutions containing 6 ml. of nitric acid, 1 to 2 grams of tartaric acid, 100 mg. of antimony, 10 mg. of arsenic, 5 mg. of iron, 10 mg. of tin, 5 mg. of cadmium, and known amounts of lead, copper, and bismuth, all as nitrates, were diluted to 250-ml. volume and analyzed as described in Procedure A. The anolyte was lead nitrate solution containing 3 per cent of nitric acid in which the lead concentration approximated that of the catholyte. The results are shown in Tables I and II.

Synthetic samples containing 15 grams of lead nitrate, 8 ml. of concentrated nitric acid, 1 gram of tartaric acid, and known amounts of copper, bismuth, silver nitrate, and tartar emetic were prepared and diluted to 150 ml. The solutions

TABLE IV. DETERMINATION OF BISMUTH AND COPPER IN LEAD-TIN ALLOYS FOLLOWING REMOVAL OF SILVER

Copper Present	Copper Found	Bismuth Present	Bismuth Found	Copper and Bismuth Present	Copper and Bismuth Found	Silver Present
Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
11.0	11.2
11.0	11.2	5
4.4 ^a	4.4	5.0	5.0	9.4	9.4	5
11.0 ^a	10.9	5.0	5.3	16.0	16.2	...
4.4 ^b	4.5	2.5	2.7	6.9	7.2	3
5.0	4.7	5.0	5.0	10.0	9.7	...
5.0	4.8	5.0	5.7	10.0	10.5	...
5.0	4.9	5.0	4.8	10.0	9.7	...
5.0	5.1	2.5	2.5	7.5	7.6	...
12.5	13.0	5.0	5.0	17.5	18.0	...
5.0 ^c	4.7
5.0	4.3	5.0	5.1	10.0	9.4	4
5.0	4.8	5.0	5.1	10.0	9.9	2
5.0	4.8	5.0	4.9	10.0	9.7	2
5.0	5.0	5.0	5.1	10.0	10.1	2
5.0	3.8	5.0	5.9	10.0	9.7	5
5.0	5.1	5.0	5.0	10.0	10.1	1

^a 100 mg. of antimony as tartar emetic added with the standard copper.
^b 10 mg. of tellurium (dissolved in HNO₃) added with the copper.
^c 100 mg. of arsenic trioxide added with the copper.

TABLE V. PRECISION OF METHOD APPLIED TO TYPICAL SAMPLES

Sample Designation	Copper %	Deviation from Mean	Bismuth %	Deviation from Mean
Commercial lead	0.065	+0.001	0.014	-0.0005
	0.063	-0.001	0.015	+0.0005
Av.	0.064	±0.001	0.0145	±0.0005
No. 1, 1% antimony lead	0.056	-0.0002	0.124	+0.001
	0.056	-0.0002	0.124	+0.001
	0.056	-0.0002	0.122	-0.001
	0.057	+0.0008	0.122	-0.001
Av.	0.0562	±0.0004	0.123	±0.001
No. 2, 1% antimony lead	0.060	+0.0007	0.064	+0.001
	0.059	-0.0003	0.060	-0.003
	0.059	-0.0003	0.065	+0.002
Av.	0.0593	±0.0004	0.063	±0.002
40-60 lead-tin solder	0.022	-0.001	0.038	+0.002
	0.024	+0.001	0.034	-0.002
Av.	0.023	±0.001	0.036	±0.002

were boiled to remove nitrous acid fumes, and were then diluted to approximately 300 ml., cooled to 65° C., and analyzed as described in Procedure A. The results are shown in Table III.

Ten grams of a 50:50 lead-tin alloy were dissolved in a nitric-hydrofluoric acid mixture as recorded in Procedure B. The solution was diluted, 2 grams of tartaric acid were added, and the solution was electrolyzed at 65° to 75° C. in the lead-platinum cell. The plate was discarded. Known amounts of copper, bismuth, and silver as nitrates were added to the purified solution. Copper and bismuth were then determined as described in Procedure B. (See Table IV.)

The data presented in Tables I to V indicate that there are no significant constant errors in the method. The precision of Procedure B, in which hydrofluoric acid is used, is somewhat lower than Procedure A because of the poorer character of the plates obtained in this solution. In Procedure B there is also more danger of loss of metal by re-solution during the washing of the plate.

The precision limits of Procedure A are as follows: bismuth, ±50 parts per thousand when the bismuth content of the sample is 0.05 per cent; copper, ±30 parts per thousand when the copper content is 0.05 per cent.

The precision limits of Procedure B are as follows: bismuth, ±100 parts per thousand when the bismuth content is 0.05 per cent; copper, ±75 parts per thousand when the copper content is 0.05 per cent.

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Separation of Strontium, Barium, and Lead from Calcium and Other Metals

By Precipitation as Nitrates

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IN THE quantitative separation of strontium from calcium there has always been considerable difficulty due to the fact that most of the properties of strontium are very closely related to those of calcium. Thus, although the determination of either strontium or calcium alone is easily carried out, the task of determining them when taken together presents greatly increased difficulty.

By extracting the mixture of anhydrous nitrates with absolute alcohol, in which strontium nitrate is not very soluble, Stromeyer (5) separated strontium from calcium. Rose (4) improved this method by using a mixture of equal parts of absolute alcohol and anhydrous ether, in which strontium nitrate is much less soluble than in alcohol alone. With certain modifications introduced by Fresenius (1), this method is the one most used today. Rawson (3) suggested the use of concentrated nitric acid as the extracting solvent.

Since precipitation methods are known to be superior to extraction methods, both in accuracy and ease of manipulation, it seemed desirable to develop such a method for the separation of strontium from calcium and other metals.

Preparation and Standardization of Solutions

C. P. strontium nitrate was dissolved in water and filtered to remove any insoluble impurities. The strontium was precipitated as the nitrate by the slow addition, with stirring, of enough 70 per cent nitric acid to bring the acid concentration of the solu-

tion up to about 40 per cent. The strontium nitrate was filtered off, washed with 40 per cent nitric acid, dissolved, and then reprecipitated a second time in a similar manner. The solution of strontium nitrate was standardized by pipetting 10-ml. samples into weighed crucibles, adding a few drops of nitric acid, and evaporating to dryness on a very low-temperature hot plate. The strontium nitrate was then dried 2 hours at 130° to 140° C., and weighed. This standardization was checked by precipitating 10-ml. samples as the sulfate with a tenfold excess of sulfuric acid from a 50 per cent alcohol solution. After standing 12 hours, the precipitate of strontium sulfate was filtered through a Gooch crucible and dried 1 hour in a muffle heated to 500° C. The results obtained by the two methods agreed within 0.1 mg.

Solutions of barium nitrate and lead nitrate were purified in a similar manner and standardized by evaporating to dryness and weighing as the nitrates.

The calcium nitrate solution was prepared from reagent quality calcium carbonate by dissolving it in dilute nitric acid. It was purified by adding 100 per cent nitric acid until the acid concentration was 80 or 81 per cent, the volume being such that a small amount of calcium nitrate was precipitated. After standing 0.5 hour the precipitated calcium nitrate (along with any barium or strontium nitrates that might have been present) was filtered off and discarded. The filtrate was evaporated to dryness to remove the nitric acid, and the calcium nitrate was then dissolved in water. The solution was standardized by precipitating 10-ml. samples as oxalate, followed by ignition at 500° C. to the carbonate.

Although fuming nitric acid as purchased could be used successfully for obtaining the desired acid concentration, in most of this work freshly prepared 100 per cent nitric acid was employed. This was prepared by distilling a mixture of c. p. sodium nitrate

and c. p. concentrated sulfuric acid in an all-glass distilling apparatus, the flask having a capacity of 2 liters. A convenient charge consisted of 500 grams of sodium nitrate and 500 ml. of sulfuric acid.

Experimental

Attempts were first made to precipitate strontium nitrate from solution in an organic solvent. The general method used was to evaporate a sample of strontium nitrate to dryness with an excess of perchloric acid and dissolve the strontium perchlorate in the organic solvent. Strontium was then precipitated as the nitrate by the slow addition of a mixture of the solvent and 100 per cent nitric acid. The solvents tried were a mixture of absolute alcohol and anhydrous ether, normal butyl alcohol, a mixture of normal butyl alcohol and anhydrous ether, tertiary butyl alcohol, carbitol, and butyl carbitol. Incomplete precipitation and the formation of slimy, unfilterable precipitates caused this work to be abandoned.

It was found that dry strontium nitrate could be dissolved in a very little water and was precipitated in a dense granular form by the addition of nitric acid, whereas calcium nitrate proved to be much more soluble. The precipitate showed no tendency whatever to stick to the sides of the beaker, and was readily washed into the filtering crucible with a few jets of acid of the same concentration as that used for the precipitation.

The wash bottle was a 250-ml. Erlenmeyer flask fitted with a two-hole rubber stopper. A rubber bulb furnished the necessary air pressure. The rubber bulb and stopper are attacked slowly by the nitric acid vapors but, if rinsed after being used, they last a long time.

The solutions were filtered through Gooch crucibles with rather thick pads. The precipitates were dissolved out and the pads used repeatedly. In dissolving the precipitates, hot water with a little nitric acid proved to be more satisfactory than hot water alone, especially if metals other than strontium were present. The strontium nitrate precipitate was dried 2 hours at 130° to 140° C., but longer drying does no harm.

The concentrations of the nitric acid solutions were obtained from tables (2), after determining the specific gravity of the pure solutions by means of a hydrometer having a range of 1.4 to 1.6. (For concentrations below 70 per cent a hydrometer with a range of 1.2 to 1.4 was used.) A few specific gravity determinations were made with a pycnometer and the values were found to check those obtained by the hydrometer method within 0.002. We may assume, then, that the acid concentration is always within 1 per cent of the stated value, and usually within 0.5 per cent.

Precipitations were first made by dissolving the dry salts in a definite volume of water, adding a known amount of 70 per cent (ordinary concentrated) nitric acid, which caused most of the strontium nitrate to precipitate, and then adding a definite amount of 100 per cent nitric acid to bring the acid concentration to the desired value. It was simpler, however, to dissolve the dry salts in a definite volume of water and add enough 100 per cent nitric acid, drop by drop, with constant stirring, to bring the acid concentration up to the desired value. This was determined by adding to the proper volume of water increasing amounts of acid and determining the specific gravity with a hydrometer, applying a temperature correction. It is convenient to make all the additions from a buret. If 70 per cent nitric acid is used, each bottle must be tested, likewise the c. p. fuming nitric acid of commerce.

Precipitation was complete within 30 minutes, except that for very small amounts it was necessary to stir the solution mechanically for 45 minutes.

EFFECT OF VARYING ACID CONCENTRATION. In determining the effect of acid concentration all precipitates stood 0.5 hour or more before filtering, were transferred and washed with about 18 ml. of acid of the same concentration as that used during the precipitation, were then dried for 2 hours at 130° to 140° C., and weighed. The volume during precipitation was about 18 ml. The results are shown in Table I.

As an additional check the filtrates and washings were evaporated to dryness and taken up with water. Any barium

or strontium present was precipitated as sulfate, the latter from a 50 per cent alcohol solution. No barium sulfate could be detected in the filtrates from acid concentrations of 76 per cent or higher. With strontium a very faint turbidity was noticed with 70 per cent acid, less with 80 per cent, and none with higher concentrations. In the case of lead, noticeable precipitates were obtained with ammonium sulfide in all filtrates up to, and including, the 80 per cent acid. In the others no precipitate settled out, but the solutions darkened considerably. There was no difference in the amount of darkening between those obtained with the 83 per cent and the 87 per cent acids, but that with the 82 per cent was somewhat darker. In general, the solubility of lead nitrate in 84 per cent nitric acid corresponds to about 0.1 mg. of lead per 20 ml. The solubility increases considerably with higher temperatures, but is reduced to a negligible amount when the solution is cooled in ice. It would seem, then, that 76 per cent nitric acid suffices for barium, but 80 per cent acid is required for strontium, and 84 per cent for lead.

TABLE I. EFFECT OF ACID CONCENTRATION ON PRECIPITATION OF STRONTIUM, BARIUM, AND LEAD NITRATES

(All precipitations were made in a volume of about 18 ml. at 20° to 25° C. The precipitates were transferred and washed with about 18 ml. of acid of the same concentration as that used for the precipitation.)

Acid, per cent	66	69	74	78	80	83	85	87
Sr found, error, mg. (57.9 mg. taken in each case)	...	-1.3 -1.7	-0.3 -0.3	0 -0.1	0 0	+0.1 0	0 0	...
Ba found, error, mg. (56.6 mg. taken in each case)	-0.8 -0.9	...	0 -0.1	0 -0.1	0 -0.1	0 -0.1	0 -0.1
Pb found, error, mg. (101.7 mg. taken in each case)	-8.8 -9.5	...	-1.3 -1.4	-0.9 -0.7	-0.2 -0.4	-0.2 -0.1	-0.1 -0.1

Using 77 per cent nitric acid, in which the solubility of strontium nitrate is appreciable, a comparison of the solubility of strontium nitrate in both the precipitating and the wash solutions was made. About 140 mg. of strontium nitrate were dissolved in a little water and the acid concentration was brought up to 77 per cent, the volume being 100 ml. After standing 0.5 hour the precipitate was filtered off and the strontium in the filtrate was determined as sulfate. The precipitate in the crucible was then washed with 100 ml. of 77 per cent nitric acid, and the strontium determined in the washings. The strontium sulfate in each case weighed 0.7 mg., indicating that the wash solution becomes saturated with the nitrate.

EFFECT OF TEMPERATURE. Since the separation of strontium from certain metals might be improved by an increase in temperature, a few determinations were made at 50° and 70° C., these temperatures being maintained for 0.5 hour after precipitation, when the solution was filtered and washed with acid at room temperature. The results in Table II show that temperatures up to 70° C. may be used without causing loss of strontium nitrate. Temperatures above 70° C. were not tried, because above this the nitric acid fumes off rather rapidly.

TABLE II. PRECIPITATION OF STRONTIUM NITRATE AT VARIOUS TEMPERATURES FROM 80 PER CENT NITRIC ACID

[Sr(NO ₃) ₂ taken, 149.3 mg. = 61.8 mg. of Sr]		
Temperature ° C.	Sr(NO ₃) ₂ Found Mg.	Error, Sr Mg.
25	149.6	+0.1
	149.4	0
	149.2	0
50	149.2	0
	149.5	+0.1
70	149.4	0

EFFECT OF OTHER ANIONS. No effort was made to determine an all-inclusive list of anions that might be present in the determination of strontium. However, as it was felt that chloride and perchlorate would be frequently encoun-

tered, tests were made in their presence. The amounts of these acids taken were greatly in excess of that required to convert all the strontium to chloride and perchlorate, and were added after evaporation to dryness, so that the full amount of acid was present during precipitation. Precipitation was made in 80 per cent nitric acid in a volume of 18.2 ml. Upon taking 0.75 ml. of concentrated hydrochloric acid and 139.9 mg. of strontium nitrate, 140.0 and 140.1 mg. of strontium nitrate were found. When 149.3 mg. of strontium nitrate were taken with 0.75 ml. of 70 per cent perchloric acid, 149.5 and 149.3 mg. of strontium nitrate were found.

Evidently these ions exert no harmful effect on the determination of pure strontium.

TABLE III. SOLUBILITY OF CALCIUM NITRATE IN NITRIC ACID

Acid Concentration %	Calcium Dissolved Mg./ml.
77	26.5
79	10.0
81	5.0
83	1.9
85	1.1

SOLUBILITY OF CALCIUM NITRATE IN NITRIC ACID. The solubility of calcium nitrate in nitric acid of various concentrations was determined by putting an excess of finely pulverized calcium nitrate in glass-stoppered cylinders containing the nitric acid. The mixture was kept in a thermostat at 25° C. for several hours with frequent shaking. Samples of 50 ml. were pipetted out, the nitric acid was evaporated, and the calcium determined by precipitation as the oxalate followed by ignition at 500° C. to the carbonate. The results, shown in Table III, indicate that as low an acid concentration as possible should be used in separating strontium from calcium.

Separation of Strontium from Calcium

It was found essential to add the nitric acid drop by drop with constant stirring, in order to avoid carrying down appreciable amounts of calcium. Separations of strontium made by the addition of the acid in a stream from a buret with a little stirring gave results 1.7 mg. too high, while identical separations made with drop-by-drop addition of the acid with constant vigorous stirring gave correct results.

The greater the volume of the solution at the time of precipitation, the better are the separations obtained. However, because of the slight solubility of strontium nitrate and the greater ease in transferring the precipitate from a small beaker, total volumes under 40 ml. were usually employed and a 50-ml. beaker was used. Best results were obtained by precipitating the bulk of the strontium with 70 per cent nitric acid and then using 100 per cent acid to bring the concentration up to the desired value. However, it is simpler to eliminate the use of the 70 per cent acid, and results practically as good may be obtained using only 100 per cent acid, provided it is added very slowly and with vigorous (preferably mechanical) stirring. A solution in which the acid concentration is 80 per cent may be obtained by dissolving the salt in 10.0 ml. of water and adding 26.0 ml. of 100 per cent nitric acid.

Separations were made in which the time of standing after precipitation was varied from 0.5 to 5 hours. There is a slight downward trend in the amount of calcium carried down as the time of standing is lengthened. Evidently on standing some of the co-precipitated calcium nitrate is gradually dissolved.

Separations were tried at elevated temperatures, but no appreciable advantage is gained by precipitating hot.

Separations were made using various acid concentrations.

As was to be expected, the lower acid concentrations gave better separations, but any concentration in the range of 79 to 81 per cent is satisfactory. Above 81 per cent the solubility of calcium nitrate is too small, and below 79 per cent the solubility of strontium nitrate becomes appreciable.

Table IV shows the results of some separations of strontium from calcium. The dry nitrates were dissolved in 10.0 ml. of water, and the strontium nitrate was precipitated by adding 26.0 ml. of 100 per cent nitric acid drop by drop with mechanical stirring. This gave an acid concentration of 80 per cent. After the addition of the acid the solution stood 0.5 hour, before filtering through Gooch crucibles, the precipitate being transferred with jets of 80 per cent nitric acid, then washed 10 times in the crucibles with approximately 1-ml. portions of 80 per cent nitric acid. The strontium nitrate was dried 2 hours at 130° to 140° C. In making double precipitations the precipitates were dissolved directly into a beaker placed under a bell jar, using hot water which had been slightly acidified with nitric acid. In each case pure strontium was carried through the same process to ensure that the results obtained were not due to compensating errors.

TABLE IV. SEPARATION OF STRONTIUM FROM CALCIUM

Taken		First Precipitation		Second Precipitation	
Sr	Ca	Found, Sr	Error, Sr	Found, Sr	Error, Sr
Mg.	Mg.	Mg.	Mg.	Mg.	Mg.
2.1 ^a	50	2.8	+0.7	2.0	-0.1
		2.8	+0.7	2.0	-0.1
		3.2	+1.1	2.3	+0.2
2.1 ^{a,b}	500	4.0	+1.9	2.3	+0.2
		2.1	0	2.0	-0.1
2.1 ^a	None	2.1	0	2.0	-0.1
		12.9	+0.5	12.4	0
12.4	50	12.8	+0.4	12.3	-0.1
		12.4	0	12.3	-0.1
12.4	None	12.3	-0.1	12.3	-0.1
		62.0	+0.3	61.5	-0.2
61.7	50	61.9	+0.2	61.6	-0.1
		61.7	0	61.6	-0.1
61.7	None	61.7	0	61.7	0
		154.6	+0.2	154.2	-0.2
154.4	50	154.5	+0.1	154.2	-0.2
		154.4	0	154.4	0
154.4	None	154.4	0	154.3	-0.1
		929.7	+1.0	928.7	0
928.7	50	929.9	+1.2	928.7	0
		928.8	+0.1	928.7	0
928.7	None	928.6	-0.1	928.6	-0.1
		61.7	0	Second pptn. not needed	
61.7	25	61.7	0		
		62.7	+1.0	61.6	-0.1
61.7	125	62.7	+1.0	61.7	0
		65.7	+4.0	61.8	+0.1
61.7 ^b	500	65.3	+3.6	61.7	0
		61.6	-0.1	61.5	-0.2
61.7 ^b	None	61.6	-0.1	61.6	-0.1

^a Mechanically stirred for 45 minutes after precipitation.

^b 30 ml. of water and 78 ml. of 100 per cent nitric acid, giving 80 per cent acid for the first precipitation; second precipitation, 10 ml. of water, 26 ml. of 100 per cent acid.

Various amounts of strontium may be separated from 25 mg. of calcium with only one precipitation. If more than 25 mg. of calcium are present double precipitations are necessary, and if the amount of calcium is very large the volume of the solution must be increased.

Separation of Strontium from Metals Other than Calcium

Solutions of many metals were made up, usually from the nitrates. The solutions were made from c. p. chemicals, and as first prepared were not purified in any way. If high results were obtained in a separation, the solution of the metal was purified by treatment with 80 per cent nitric acid, filtering off any precipitate that was obtained. The solutions were not analyzed as to metal content, but were probably accurate to within 10 per cent.

Generally the dry salts were dissolved in 3.0 ml. of water and precipitated with 5.5 ml. of 71 per cent nitric acid, and the concentration was brought to 80 per cent by the addition of 10.0 ml. of 100 per cent nitric acid. The precipitate was allowed to stand 0.5 hour, and then was transferred and washed with about 18 ml. of 80 per cent nitric acid, after which it was dried for 2 hours at 130° to 140° C.

Solution of the salts in 3.0 ml. of water was readily accomplished by adding 1.0 ml. of 71 per cent nitric acid and heating a few minutes. In the list of metals separated from strontium, the

TABLE V. SEPARATION OF STRONTIUM FROM VARIOUS METALS
[In each case $\text{Sr}(\text{NO}_3)_2$ taken, 149.3 mg. = 61.8 mg. of Sr]

Salt Added	Metal Content Mg.	Error, Sr Mg.
$\text{Al}(\text{NO}_3)_3$	25	+0.2
$\text{Al}(\text{NO}_3)_3$	75 ^a	0
NH_4NO_3	500	-0.1
SbCl_3	500 ^b	+0.1
H_3AsO_4	500	0
$\text{Be}(\text{NO}_3)_2$	500	-0.1
$\text{Bi}(\text{NO}_3)_3$	500	+0.2
$\text{Ca}(\text{NO}_3)_2$	25	+0.2
$\text{Cd}(\text{NO}_3)_2$	500	+0.1
$\text{Ce}(\text{NO}_3)_4$	500	-0.1
$\text{Cr}(\text{NO}_3)_3$	100	+0.5
$\text{Co}(\text{NO}_3)_2$	500	+0.3
$\text{Cu}(\text{NO}_3)_2$	250	+0.1
$\text{Cu}(\text{NO}_3)_2$	500 ^a	0
$\text{Fe}(\text{NO}_3)_3$	500	-0.1
$\text{La}(\text{NO}_3)_3$	500	-0.1
LiNO_3	150	+0.1
$\text{Mg}(\text{NO}_3)_2$	500	0
$\text{Mn}(\text{NO}_3)_2$	500	+0.1
$\text{Hg}(\text{NO}_3)_2$	500	0
$\text{Ni}(\text{NO}_3)_2$	2000	0
KNO_3	500	+0.5
H_2SeO_4	500	+0.4
AgNO_3	150	+0.1
NaNO_3	300	0
H_2TeO_3	75	+0.2
TiCl_3	500	+0.2
TiNO_3	500	+0.3
SnCl_4	500	+0.2
$\text{UO}_2(\text{NO}_3)_2$	500	0
$\text{Zn}(\text{NO}_3)_2$	500	+0.1
		0

^a Precipitated at 70° C.
^b 1.5 ml. of HCl added.

TABLE VI. SEPARATION OF BARIUM FROM VARIOUS METALS
[In each case $\text{Ba}(\text{NO}_3)_2$ taken, 107.7 mg. = 56.6 mg. of Ba]

Salt Added	Metal Content Mg.	$\text{Ba}(\text{NO}_3)_2$ Found Mg.	Error, Ba Mg.
$\text{Bi}(\text{NO}_3)_3$	500	107.7	0
$\text{Ca}(\text{NO}_3)_2$	125	107.6	0
$\text{Cd}(\text{NO}_3)_2$	500	107.9	+0.1
$\text{Ni}(\text{NO}_3)_2$	500	107.6	0
Pure $\text{Ba}(\text{NO}_3)_2$...	107.9	+0.1
		107.7	0
		107.8	0
		107.8	0
		107.6	0
		107.5	-0.1

only ones which could not be dissolved in this volume were 500 mg. of beryllium nitrate, 500 mg. of ferric nitrate, and 2000 mg. of nickel nitrate. For these amounts of beryllium, iron, and nickel, larger initial volumes were used, the amount of 71 per cent acid being decreased, and the 100 per cent increased, in order to keep the final volume the same.

In the case of antimony and tin, as it was found advantageous to have some hydrochloric acid present, the salts were dissolved in a mixture of 1.5 ml. of water and 1.5 ml. of concentrated hydrochloric acid.

Nearly all precipitations were made at room temperature but in some cases a large temperature effect was noticed. This was especially true with copper and aluminum, so a few

separations from these metals were made at 70° C. The solutions were allowed to stand for 0.5 hour at the same temperature, after which they were filtered through a warm crucible and washed with acid at room temperature.

The metals from which separations were made, as shown in Table V, are the largest amounts possible in a volume of 18.5 ml. of 80 per cent nitric acid, with the exception of those metals from which the separation of 500 mg. or more was possible. No amounts greater than 500 mg. were tried except in the case of nickel, where the maximum used was 2000 mg. If larger volumes were used, separations from larger amounts of the metals would be possible.

The only metal tried from which strontium could not be separated was titanium (except for barium and lead which were quantitatively precipitated).

RECOMMENDED PROCEDURE. Evaporate the metallic chloride, perchlorate, or nitrate (preferably the latter) to dryness; dissolve in 10.0 ml. of water; precipitate the strontium nitrate by adding 26.0 ml. of 100 per cent nitric acid, drop by drop, with constant (preferably mechanical) stirring; allow to stand 0.5 hour; filter through a Gooch crucible, transferring the precipitate with a jet of 80 per cent nitric acid, and washing ten times with acid of the same concentration, using about 1 ml. each time; dry at 130° to 140° C. for 2 hours; weigh as $\text{Sr}(\text{NO}_3)_2$. Larger volumes and double precipitations may be used if necessary.

Determination of Barium and Separation from Other Metals

The precipitate of barium nitrate is of the same dense crystalline form that characterizes strontium nitrate, and it is reasonable to assume that barium may be separated from all the metals from which strontium may be separated. Since a lower acid concentration may be used for barium, even better separations would probably be possible. Table VI shows the results of a few separations that were made.

The dry salts were dissolved in 5.0 ml. of water. The barium nitrate was partially precipitated by the slow addition, with stirring, of 3.0 ml. of 70 per cent nitric acid, after which 11.0 ml. of 100 per cent acid were added in the same manner to bring the acid concentration up to 76 per cent. After standing 0.5 hour the barium nitrate was filtered off, washed ten times with 76 per cent nitric acid, and dried for 2 hours at 130° to 140° C.

It did not seem necessary to try other separations. Barium can undoubtedly be separated from all the metals from which strontium was separated (Table V).

Determination of Lead and Separation from Other Metals

Table VII shows the results of a few separations of lead from various metals.

The dry salts were dissolved in 2.5 ml. of water, and the acid concentration was brought to 84 per cent by the drop-by-drop addition of 5.0 ml. of 70 per cent nitric acid and 13.0 ml. of 100 per cent acid. After standing 0.5 hour at room temperature, the lead nitrate was filtered off, washed ten times with small portions of 84 per cent nitric acid, and dried for 2 hours at 135° C.

Because the presence of chloride gives low results in the determination of lead, this must be absent. This fact prevents the separation of lead from antimony and tin. A separation from all the other metals shown in Table V would no doubt be possible.

In some cases at least, separations are made from highly supersaturated solutions of the metals. For instance, in the separation of lead from copper, a crystal of copper nitrate was added to the filtrate and caused a large amount of copper nitrate to precipitate. This was filtered, dried, and with an indefinite amount of water of crystallization weighed 0.7 gram.

TABLE VII. SEPARATION OF LEAD FROM VARIOUS METALS

[In each case $\text{Pb}(\text{NO}_3)_2$ taken, 162.5 mg. = 101.7 mg. of Pb]

Salt Added	Metal Content Mg.	$\text{Pb}(\text{NO}_3)_2$ Found Mg.	Error, Pb, Mg.
H_3AsO_3	500	162.3	-0.1
		162.4	-0.1
		162.7	+0.1
$\text{Bi}(\text{NO}_3)_3$	500	162.9	+0.2
		163.0	+0.3
$\text{Ca}(\text{NO}_3)_2$	15	162.9	+0.2
		162.2	-0.2
$\text{Cd}(\text{NO}_3)_2$	500	162.3	-0.1
		162.2	-0.2
$\text{Cu}(\text{NO}_3)_2$	300	162.2	-0.2
		162.4	-0.1
$\text{Hg}(\text{NO}_3)_2$	500	162.5	0
		162.4	-0.1
Pure $\text{Pb}(\text{NO}_3)_2$...	162.4	-0.1

Summary

Attempts to separate strontium from calcium by precipitation of strontium nitrate with nitric acid in organic solvents resulted in incomplete precipitation and slimy, unfilterable precipitates.

Strontium nitrate can be completely precipitated in a dense, crystalline form from a water solution, and separated from twenty-eight metals by the very slow addition of 100 per cent nitric acid until the resultant solution contains not

less than 79 per cent: to separate barium from the same metals, 76 per cent acid suffices; to separate lead, 84 per cent is necessary, but chloride makes impossible a separation of lead from tin and antimony.

The precipitate should stand at least 30 minutes before filtering; if it is very small, the solution should be stirred mechanically for 45 minutes. The nitrate is dried 2 hours at 130° to 140° C.

Temperatures up to 70° C. do not increase appreciably the solubility of strontium nitrate but may increase that of other nitrates.

The solubility of calcium nitrate decreases rapidly with increasing acid concentrations. A maximum of 80 per cent acid is recommended.

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Determination of Phthalate Plasticizers

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WHEN the diamyl, dibutyl, diethyl, and dimethyl esters of phthalic acid are used to plasticize cellulose nitrate they may be determined by extraction and saponification. However, if the cellulose nitrate plastic also contains aromatic nitro derivatives, such as those of benzene, toluene, and xylene, the determination of the phthalate plasticizer becomes more difficult. These nitro compounds are soluble in the plasticizers and are also mutually soluble with them in solvents. They therefore cannot be separated by difference in solubilities. When the alkali is added for the saponification of the ester plasticizer, in the presence of these nitro compounds, colored additive compounds of the alkali and nitro derivatives are formed (4). These colored compounds cannot be separated from the plasticizer by solvents and only a trace of them is necessary to interfere with the titration of the alkali after saponification. Therefore, a method for the determination of the phthalate plasticizers, in the presence of aromatic nitro derivatives, was sought.

Experimental

Unable to determine the phthalate esters in this mixture by saponification, a gravimetric method was developed.

Barium phthalate is regularly referred to in organic chemistry texts (1, 2) as an insoluble salt of phthalic acid. It will not precipitate when barium chloride is added to acid solutions of phthalic acid, but phthalic acid itself is precipitated. The solution must be neutral to precipitate barium phthalate. Following the procedure of Ekeley and Banta (3), barium nitrate was added to a solution of sodium phthalate. On boiling, a barium salt was precipitated, which analyzed 51.41 per cent barium oxide compared with 50.89 per cent barium oxide theoretical. In 100 cc. of water at 20° C., 0.2760 gram of this salt was found to be soluble, in spite of the constant reference to barium phthalate in the literature as an insoluble salt of phthalic acid. Since barium phthalate

precipitates only in neutral solutions, allowing the precipitation of other barium salts, and because of its solubility, it was eliminated as a means of precipitating phthalic acid.

Precipitation of phthalic acid as lead phthalate proved to be more favorable than the barium precipitation. Lead phthalate was prepared from phthalic anhydride and lead nitrate, and analyzed 56.55 per cent lead compared with 55.82 per cent lead theoretical. It was also made from saponified dibutylphthalate and lead nitrate and upon analysis gave 55.94 per cent lead. Lead phthalate is a white crystalline compound, of which 0.0020 gram is soluble in 100 cc. of water at 20° C. It is soluble in nitric acid but insoluble in dilute acetic acid. Because of its low solubility and ease of formation, lead phthalate was adopted as a means of precipitation of phthalic acid. Lead acetate was later used in place of lead nitrate, as the nitric acid left from this reagent interfered with the precipitation of lead phthalate. It was also decided to reprecipitate lead phthalate as lead sulfate to eliminate errors that might be introduced by insoluble organic compounds.

The phthalic acid could not be liberated quantitatively by the saponification of the ester in the presence of nitro compounds, therefore it was liberated from the ester plasticizer by the oxidation of the aliphatic side chains by nitric acid. Crystals were obtained by adding 30 cc. of concentrated nitric acid to approximately 1 gram of dibutylphthalate and evaporating to dryness on the steam bath. These crystals were identified as phthalic acid, according to Mulliken (5), by being converted to *o*-phthalanil, melting at 205° C. A trace of nitrophthalic acids was also formed. Oxalic acid was found to be present as a product of the side-chain oxidation of the phthalate esters of the higher alcohols. Oxalic acid must be removed before the lead precipitation because lead oxalate has properties similar to those of lead phthalate. This removal of oxalic acid was accomplished by a second oxidation, using potassium permanganate.

At first, the nitric acid oxidation was applied to the free ester plasticizers and yields of around 55 per cent were obtained. Then, dry cellulose nitrate was also added to the phthalate plasticizer. Oxidation of this mixture increased the yields to around 75 per cent. Yields were determined from the lead precipitation of the phthalic acid after the oxidation of the ester. This increase in yields showed that the decomposition of the cellulose nitrate aided the oxidation of the phthalate plasticizer. The concentration of the nitric acid was changed to 1 to 1, as previous work by the author proved this to be the optimum dilution for the decomposition of cellulose nitrate. The effect of the cellulose nitrate decomposition indicated that the plasticizer would have to be oxidized during the oxidation of the plastic itself. The oxalic acid would be increased, but this could be easily removed with potassium permanganate along with the oxalic acid of the oxidized side chain of the ester.

The mere addition of the dry cellulose nitrate to the phthalate ester made a very heterogeneous mixture and hence 75 per cent yields were obtained. By a careful colloid of the same amount of cellulose nitrate with the same amount of the plasticizer, thereby increasing the homogeneity of the mixture, approximately 100 per cent yields were obtained. This condition likewise simulated the finished manufactured plastic. Quantitative results having been obtained, even when aromatic nitro derivatives were added, the following procedure was adopted for the determination of the phthalate plasticizers in cellulose nitrate plastics.

Procedure

Place 5 grams of the plastic in a 500-cc. boiling flask, fitted to a reflux condenser by means of a ground-glass joint (Scientific Glass Apparatus Co. No. 1400). Add 40 cc. of 1 to 1 nitric acid to the flask and reflux the mixture at the full heat of an electric flask heater (Gilmer type) until decomposition is complete and a clear solution is obtained (about 45 minutes). Reflux for about 30 minutes longer to ensure complete reaction. This oxidation must not be interrupted or the results will be low. Allow to cool and add 50 cc. of water. Remove flask from the condenser, insert a glass stopper, and cool further, with shaking, under the tap. Allow to stand for 3 hours. Insoluble nitro compounds will settle out, if present.

Filter through a No. 42 Whatman filter paper into a 400-cc. beaker, washing three or four times with cold water. If the volume is more than approximately 100 cc., place on a hot plate and evaporate to this volume. Place beaker on the steam bath and add small amounts of potassium permanganate to remove the oxalic acid. Just a few crystals on the end of a weighing spatula are added each time, and the reaction is allowed to complete itself before the next addition. This is continued until a large precipitate of manganese dioxide persists, and, apparently, does not clear up at the heat of the steam bath. Filter off the manganese dioxide, while the solution is hot, into a 250-cc. beaker, and wash with hot water. Place the beaker on a slow hot plate and evaporate nearly to dryness; then bring to dryness on the steam bath to remove the nitric acid. Lead phthalate is soluble in nitric acid.

After evaporation, the beaker contains phthalic acid and manganese salts. Dissolve these in 50 cc. of warm water, add 20 cc. of 10 per cent lead acetate solution, containing 10 cc. of acetic acid per 100 cc. of solution. Heat on a hot plate, low heat, until the volume is about 50 cc. and allow to stand overnight. Lead phthalate will precipitate as a white crystalline precipitate. Filter, using No. 42 filter paper and washing three or four times with cold water from the beaker onto the filter. The volume of the washings should be kept at a minimum, about 20 cc. In some cases, lead phthalate crystals will adhere to the beaker. Do not attempt to remove these with a policeman, but allow them to remain in the beaker, as they have been washed free of lead acetate. Add 15 cc. of 1 to 1 nitric acid to the beaker, dissolving these crystals. Now place a 400-cc. beaker beneath the funnel containing the lead phthalate, and pour the nitric acid solution from the 250-cc. beaker onto the filter paper. When the solution of lead phthalate is practically complete, puncture the paper with the stirring rod and wash the contents into the 400-cc. beaker. Then add 10 cc. of sulfuric acid, precipitating lead sulfate. Evaporate the nitric acid completely

and take up in 100 cc. of one part alcohol and one part water. Allow to stand 2 hours, filter through a Gooch crucible, and weigh the lead sulfate. The weight of lead sulfate is calculated to the phthalate plasticizer sought, by one of the following factors:

PbSO₄ to diamylphthalate, 1.0096
PbSO₄ to dibutylphthalate, 0.9166
PbSO₄ to diethylphthalate, 0.7324
PbSO₄ to dimethylphthalate, 0.6401

Application of the above method to known weights of the plasticizers colloid with known weights of cellulose nitrate in the laboratory gave the results in Table I.

Commercial plastics of known composition were analyzed by three operators, using the method herein submitted, and gave the results in Table II.

TABLE I. KNOWN WEIGHTS OF PHTHALATE PLASTICIZERS COLLOIDED WITH CELLULOSE NITRATE

Phthalate Plasticizer	Added Per cent	Found Per cent
Diamylphthalate	5.82	5.75
	4.97	4.94
	4.89	4.93
Dibutylphthalate	6.81	6.78
	7.02	7.00
	5.46	5.41
Diethylphthalate	4.00	4.06
	4.00	3.95
	4.00	3.99
Dimethylphthalate	5.97	6.00
	5.88	5.91
	5.39	5.31

TABLE II. ANALYSIS OF PLASTICS

Plasticizer Added Per cent	Plasticizer Found Per cent
4.85	4.80
	4.86
4.00	3.96
	4.02
2.93	2.89
	2.87

These results show that the phthalate plasticizers in cellulose nitrate plastics may be determined, in the presence of color-forming nitro derivatives, by the direct oxidation of the ester and the precipitation as the lead salt. It was also found that aromatic nitroamines did not interfere.

Acknowledgment

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The opinions or assertions contained in this article are the private ones of the writer and are not to be construed as official or reflecting the views of the Navy Department or the naval service at large.

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Determination of Semi-Microquantities of Phosphates

In the Form of a New Complex Compound, $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{H}_3\text{PMo}_{12}\text{O}_{41}$, and Some Observations on Analogous Arsenic and Germanium Compounds

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A new complex compound, $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{H}_3\text{PMo}_{12}\text{O}_{41}$, has been prepared and analyzed and applied to the determination of semi-microquantities of phosphate. The method has been applied to the estimation of phosphorus pentoxide in a phosphate rock, but was unsuccessful when applied to phosphorus in steel. Similar complex compounds of germanium and arsenic were investigated, but the determination of these elements could not be effected with these compounds.

THE high molecular weight and the insolubility of ammonium molybdophosphate would make this compound ideal for the gravimetric determination of phosphates, were it not for the fact that the pure compound can rarely be obtained under analytical working conditions. Baxter (1) has shown that ammonium molybdate is occluded at the moment of precipitation and that the process of occlusion continues even after precipitation is complete. In spite of these facts numerous methods for the determination of phosphates employing this compound are to be found in the literature; in most of these procedures satisfactory results are obtained only by rigidly adhering to the conditions of precipitation established by the authors and by using an empirical factor. It should be mentioned, however, that Ishibashi (8) has published a method in which the theoretical conversion factor is used.

In recent years cobalt and chromium amines have been used as analytical reagents for the precipitation of certain anions. As examples the precipitation of vanadates by means of hexamine-cobalti ion (12, 13) and of ferrocyanides with the same reagent (?) may be cited. G. Spacu and his associates and C. Mahr have also devised many analytical methods for cations employing amines of various types.

In this paper a new precipitation method for phosphates based on the insolubility of nitratopentamine-cobalti dodecamolybdophosphate is described. This method, while preserving the advantage of a low conversion factor, is not subject to the disadvantages of occlusion and post-precipitation so troublesome with ammonium molybdophosphate. Some attempts to determine germanates and arsenates by similar methods are included in the discussion.

In the discussion of the properties and characteristics of heteropoly acids by Ephraim (4) is found the statement, "Characteristic precipitates are also produced with cobalt and chromium amines—e. g., $[\text{Co}(\text{NH}_3)_6]\text{X}_3$." Nowhere else has any reference to compounds of this type been found, although many phosphates and molybdates of complex amines have been prepared and analyzed. Only two amines have been found which contain both phosphoric acid

and molybdic acid. These were described by Jörgensen in 1878 (9), but they differ in both formulas and properties from the salt described below.

Several new ammine salts of dodecamolybdophosphoric acid were prepared by adding an aqueous solution of the ammine to a solution of a phosphate containing an excess of sodium molybdate and sufficient nitric acid to form the heteropoly acid. The following complex ions were used: $[\text{Co}(\text{NH}_3)_6]^{+++}$, $[\text{Cr}(\text{NH}_3)_6]^{+++}$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$, $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$, and $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{++}$. Of these the last was found to yield the most satisfactory precipitate for analytical purposes; the hexamine and chloropentamine salts were difficult to filter and wash, while the dinitrito complex gave no precipitate.

Analysis of the Compound

Samples for analysis were prepared and dried in the manner described below under the general procedure for the determination of phosphates. Ammonia was determined by distillation from a sodium hydroxide solution into an excess of standard hydrochloric acid, the excess of which was then titrated with sodium hydroxide using methyl red as indicator. Cobalt and phosphorus were determined on the same sample. The sample was dissolved in 100 ml. of water containing 3 ml. of concentrated ammonium hydroxide, and the cobalt precipitated by saturation with hydrogen sulfide. The washed sulfide was dissolved in a mixture of nitric and sulfuric acids and finally precipitated and weighed as $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ according to the method of Dakin (3). The sulfide filtrate was oxidized by evaporation with nitric acid, and the phosphorus separated by double precipitation as MgNH_4PO_4 , which was ignited to pyrophosphate for weighing. Molybdenum was determined by weighing samples into dry mercury reducers and shaking with 4 N hydrochloric acid; the solution was then filtered and titrated with standard ceric sulfate solution according to the method of Furman and Murray (5). Since these authors had not studied the effect of cobalt on the reduction of molybdenum by mercury, a check of the molybdenum content of the salt was made by the α -benzoinoxime method of Knowles (11). The samples were dissolved in a minimum of freshly prepared sodium hydroxide solution and warmed until all ammonia had been expelled. The addition of 10 ml. of concentrated sulfuric acid readily dissolved the cobaltic hydroxide, and the determination could be continued in the regular manner.

For $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{H}_3\text{PMo}_{12}\text{O}_{41}$ the following percentages are calculated:

Percentages Calculated		Percentages Found
Co	2.878	2.87, 2.82
NH ₃	4.157	4.187, 4.185
P	1.515	1.51, 1.48
Mo	56.25	56.22, 56.34, 56.25, 56.49
Volumetric		56.15, 56.39
Gravimetric		

MATERIALS AND APPARATUS. The nitratopentamine-cobaltinitrate used in this investigation was prepared by the simple method described by Jörgensen (10); cobaltous nitrate, iodine,

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nitric acid, and ammonium hydroxide are the only materials necessary. The reagent is a saturated solution of this salt, made by dissolving about 8.5 grams of the salt in 1 liter of warm water (40° C.) and stirring the solution frequently until it had cooled to room temperature. The solution was filtered to remove the precipitated salt and dust. Even in a clear glass bottle unprotected from light this solution is stable for at least a month.

Acid sodium molybdate was prepared from Kahlbaum's "molybdic acid." This material was first ignited to a dull red heat to expel ammonia and then repeatedly evaporated with concentrated nitric acid and ignited until a light yellowish green product was obtained. One hundred grams of this oxide were dissolved in a minimum quantity of freshly prepared sodium hydroxide solution; the solution was then made just acid (sulfuric acid), filtered, and diluted to 500 ml. The solution should be colorless or at most have only a very faint yellow tinge.

Some difficulty was encountered in obtaining substances of sufficient purity and of suitable composition to use in testing the method; hence a standard phosphate solution was made from silver phosphate which had been prepared in a manner similar to that used by Baxter and Jones for atomic weight work (2). After drying 15 hours at 120° C., 8.8457 grams of the silver salt were dissolved in 600 ml. of water plus 25 ml. of 6 N nitric acid. Silver chloride was precipitated by the addition of a slight excess of hydrochloric acid and the solution filtered into a calibrated 2-liter (1999-ml.) flask. The washed precipitate was dried and weighed in the usual manner to serve as a check; 9.0830 grams of silver chloride were obtained, which is the equivalent of 0.3278 mg. of phosphorus per ml. From the weight of silver phosphate taken one calculates 0.3279 mg. per ml. To check the solution further $MgNH_4PO_4$ was precipitated from two 49.91-ml. samples, yielding in both cases 0.0586 gram of pyrophosphate equivalent to 0.3271 mg. of phosphorus per ml. The value calculated from the weight of silver phosphate was taken as the standard.

For the study of the effect of foreign substances, solutions of ferric sulfate, calcium acetate, ammonium sulfate, and potassium sulfate containing 2 mg. of the cation per ml. were prepared from "reagent grade" salts. These salts gave no precipitate with acidified ammonium molybdate. The acids used during the investigation were the usual laboratory C. P. reagents.

Calibrated weights and pipets were used throughout the investigation.

Procedure for Determination of Phosphates

To the phosphate solution add 6 ml. of 6 N sulfuric acid and evaporate to 5 to 8 ml. If more than a fraction of a per cent of hydrochloric or nitric acid or any hydrofluoric acid is present, evaporate in a suitable vessel to gentle fuming; cool and dilute to 5 to 8 ml. Add 1 ml. of acid sodium molybdate solution for each milligram of phosphorus present and heat to approximately 90° C. on a hot plate. Add sufficient saturated nitratopentaminecobaltinitrate solution to color the supernatant liquid pink, then 3 to 5 ml. in excess. Stir the solution and keep it at 90° for at least 5 minutes. With less than 2 mg. of phosphorus the precipitate forms slowly; stirring and gently scratching the inside of the beaker hasten precipitation. Occasionally, especially when the quantity of cobalt reagent required is large, a flocculent pink precipitate forms which may require more than 5 minutes' digestion to convert it to the tan crystalline precipitate desired.

If the volume of solution exceeds 18 to 20 ml., it should be evaporated to this volume. Cool to room temperature and filter through a tared filtering crucible. Wash free of sulfuric acid with 0.3 N nitric acid, then once with a small quantity of water. Dry the precipitate by washing down the sides of the crucible with three 5-ml. portions of 95 per cent alcohol followed by two similar portions of ether; draw air through the crucible for 5 minutes to evaporate the ether, wipe off the outside with a clean, lintless cloth, and then allow it to stand for 30 minutes in an evacuated desiccator containing calcium chloride.

The theoretical factors are used; the weight of the precipitate multiplied by 0.01515 gives the weight of phosphorus or multiplication by 0.03468 gives the weight of phosphorus pentoxide. Representative results obtained by this procedure are shown in Table I.

The appreciable solubility of the compound necessitates keeping the volume of the solution from which it is precipitated as small as possible. Various organic liquids were added to the solution in an attempt to decrease the solubility. Ethyl and methyl alcohols added to the hot solution before precipitation reduced the amount of precipitate to a trace; if added to the cold solution after the precipitate had formed,

partial decomposition of the compound resulted with the formation of the pink flocculent molybdate of the ammine. Similar results were obtained with isopropyl alcohol and acetone. Since the volume must be kept small, the method is immediately limited to comparatively small quantities of phosphate for, when more than 16 mg. of phosphorus are to be determined, the volume of the cobalt ammine solution required to precipitate it completely is excessive.

TABLE I. DETERMINATION OF PHOSPHATE AS $[Co(NH_3)_5NO_3] \cdot H_3PMO_{12}O_{41}$

Volume of Standard Solution Ml.	Weight of Precipitate Grams	Phosphorus Found Mg.	Phosphorus Taken Mg.
1.99	0.0403	0.61	0.65
1.99	0.0412	0.62	0.65
4.99	0.1071	1.62	1.64
4.99	0.1077	1.63	1.64
10.01	0.2178	3.30	3.28
10.01	0.2181	3.30	3.28
24.94	0.5395	8.17	8.18
24.94	0.5446	8.25	8.18
49.91	1.0804	16.37	16.37
49.91	1.0791	16.33	16.37

Because of the solubility of the compound in dilute nitric acid (approximately 60 mg. per 100 ml.), the wash liquid used in the first experiments was saturated with the compound. In preparing this solution it was noticed that long shaking was necessary to attain saturation, and this slow rate of solution makes possible the use of diluted nitric acid. Equally good results were obtained with 0.3, 0.5, or even 1.0 N acid as wash liquid as with the saturated solution. For ordinary work 0.3 N acid is recommended, but when much calcium is present it is advantageous to use 0.5 N acid because of the greater solubility of calcium sulfate in the stronger acid.

The method of drying the precipitate which has been described was the only satisfactory means found. At both 105° and 160° C., the compound loses weight slowly but steadily for approximately 20 hours; during this interval the compound turns brown, probably indicating the loss of water of constitution. A slow stream of dry air blown directly into the crucible during the heating failed to shorten the time required to bring the material to constant weight, and temperatures much above 160° are unsafe since decomposition of the compound begins.

The removal of nitric and hydrochloric acid from the solution is necessary to prevent the precipitation of molybdenum oxide from the hot solution, while the presence of hydrofluoric acid prevents the formation of the heteropoly acid. The fuming with sulfuric acid must not be continued too long to avoid volatilization of metaphosphoric acid (6). Six milliliters of 6 N sulfuric acid were found sufficient and satisfactory for all determinations, but this amount could be doubled without affecting the results. A large excess of sodium molybdate does not seem to be necessary for complete precipitation; a 3- to 5-fold excess is sufficient.

Effect of Foreign Ions

With a view to applying this method to the estimation of phosphorus in phosphate rock and in alloys, the effects of iron and calcium were studied. No manipulative difficulty was encountered with iron or small amounts of calcium, but when large quantities of the latter element were present, calcium sulfate crystallized along with the phosphate precipitate. Since this compound is appreciably soluble in dilute acids, it could be dissolved out of the filtered precipitate during the washing process. At best this process is rather slow; it may be hastened somewhat by using 0.5 N nitric acid for the wash liquid and by allowing each portion to remain in contact with the precipitate for a short time before drawing it through. Results are shown in Table II.

TABLE II. DETERMINATION OF PHOSPHORUS IN THE PRESENCE OF CALCIUM AND IRON

Volume of Standard Solution Ml.	Other Ions Fe ⁺⁺⁺ Ca ⁺⁺		Weight of Precipitate Gram	Phosphorus Found Mg.	Phosphorus Taken Mg.
	Mg.	Mg.			
1.99	100		0.0434	0.66	0.65
4.99	10		0.1105	1.67	1.64
4.99	10		0.1053	1.60	1.64
4.99	50		0.1012	1.53	1.64
4.99	50		0.1137	1.72	1.64
4.99	50		0.1098	1.66	1.64
24.94	10		0.5463	8.28	8.18
24.94	50		0.5408	8.19	8.18
24.94	100		0.5424	8.22	8.18
4.99	100		0.1105	1.67	1.64
1.99		50	0.0421	0.64	0.65
10.01		50	0.2170	3.29	3.28
24.94		10	0.5428	8.22	8.18
10.01	10	10	0.2167	3.28	3.28
10.01	50	50	0.2138	3.24	3.28
1.99	50	50	0.0425	0.64	0.65

Because of the insolubility of the ammonium and potassium salts of molybdophosphoric acid, the effect of these ions was also studied. With ammonium salts and large amounts of potassium salts, the yellow precipitate forms before the addition of the cobalt ammine; in the case of potassium this precipitate gives way to the cobalt ammine precipitate, but the final precipitate obtained in the presence of ammonium salts is usually contaminated by the yellow salt. This could be ascertained microscopically if it were not already apparent to the unaided eye. The microscope failed to reveal the presence of any potassium molybdophosphate in the precipitates thrown down in solutions containing this ion; the flame test is uncertain, since molybdenum gives a red line near that characteristic of potassium. The precipitates were not examined spectroscopically. The results in the presence of ammonium and potassium ions are shown in Table III.

TABLE III. DETERMINATION OF PHOSPHORUS IN THE PRESENCE OF POTASSIUM AND AMMONIUM IONS

Phosphorus Taken Mg.	Other Ions NH ₄ ⁺ K ⁺		Weight of Precipitate Gram	Phosphorus Found Mg.	Remarks
	Mg.	Mg.			
0.65	10		0.0405	0.61	No NH ₄ salt found in precipitate
0.65	50		0.0445	..	Bright yellow precipitate
1.64	10		0.1086	1.65	Some NH ₄ salt
1.64	50		Not weighed	..	99% NH ₄ salt
0.65		20	0.0419	0.63	
0.65		50	0.0427	0.65	
0.65		100	0.0446	0.68	
3.28		20	0.2154	3.26	
3.28		50	0.2167	3.28	
8.18		10	0.5427	8.22	
8.18		50	0.5405	8.19	
8.18		100	0.6451	9.67	
8.18		100	0.5311	8.05	

Citrates, tartrates, and presumably other similar hydroxy acids prevent the complete precipitation of the phosphate by uniting with the molybdenum to form stable complexes. In the presence of 0.5 gram of either of these acids the recovery of phosphorus was never complete; usually about two-thirds of the quantity present was found.

APPLICATION TO THE ANALYSIS OF A PHOSPHATE ROCK. Thirty- to fifty-milligram samples of Bureau of Standards phosphate rock number 56 were weighed into platinum crucibles, treated with 5 ml. of 6 N nitric acid and 2 ml. of 48 per cent hydrofluoric acid, and evaporated to dryness on a hot plate. The evaporation with dilute nitric acid was repeated once. Six milliliters of 6 N sulfuric acid were then added and evaporated to the concentrated acid. When this stage was reached the acid was held at just below fuming temperature for half an hour. After cooling, the acid was diluted somewhat and filtered; hot, dilute sulfuric acid (1 part of concentrated acid to 250 parts of water) was used to wash the paper. After evaporation to small volume, the precipitation of the complex was done in the usual manner. Results of six successive analyses are shown in Table IV.

There is a tendency for the results to be low. This may be due to incomplete removal of fluorides. When the sulfuric

acid was fumed, very low percentages were found. This procedure converts a portion of the phosphoric acid to the meta acid which reverts slowly to the ortho acid; some of the meta acid may also be volatilized (6). Numerous attempts were made to avoid the use of hydrofluoric acid by treating the rock with nitric and sulfuric acids and evaporating twice to gentle fuming, removing the silica after each evaporation. In these experiments the percentage of P₂O₅ found was high as shown in Table V. These high values are probably the result of incomplete removal of silica by the short, gentle fuming; whatever silica remained would form a heteropoly acid and precipitate along with the phosphorus compound.

TABLE IV. RESULTS OF ANALYSES

Weight of Sample Gram	Weight of Precipitate Gram	P ₂ O ₅ Found %
0.0308	0.2774	31.24
0.0373	0.3351	31.16
0.0495	0.4398	30.82
0.0271	0.2449	31.35
0.0491	0.4424	31.25
0.0331	0.2960	31.02
		Average 31.14
		Bureau of Standards analysis 31.33

The results obtained by either of these procedures, while wanting somewhat in accuracy, show less spread than the results reported to the bureau by six analysts whose extreme values were 31.22 and 32.29 per cent. The method should be useful in commercial rock analysis.

Finally it should be mentioned that attempts were made to estimate phosphorus in steel by the cobalt ammine method, but without success. To avoid working with small volumes which, when 3-gram samples were taken, produced a viscous solution from which no precipitate could be obtained, 50 ml. of the cobalt ammine reagent saturated with the precipitate were added to the concentrated solution of the sample. Even prolonged shaking yielded no precipitate. Ferric and phosphate ions react in solution to form complexes, and it may be that a large excess of molybdate ion is necessary to form molybdophosphoric acid in the presence of much iron. In such circumstances the cobalt ammine method is scarcely applicable.

Attempts to Apply Amines to Determination of Germanates and Arsenates

Heteropoly acids similar to dodecamolybdophosphoric acid are formed by both germanates and arsenates, and it was thought that these ions might be determined in a manner analogous to that employed above for the determination of phosphates. Numerous experiments showed, however, that the estimation of the former was uncertain, satisfactory results being obtained in perhaps 50 per cent of the attempts; the precipitation of the latter was always incomplete. In the case of arsenates this may be attributed to the fact that the heteropoly acid forms readily only at moderately elevated temperatures at which the ammine salt is too soluble to precipitate; on cooling, the acid reverts to its components and the concentration in the solution is so low that the solubility product of the ammine salt is not exceeded. Two milligrams of arsenic as sodium arsenate gave only a few crystals when treated in the manner described for the precipitation of phosphorus. Long standing did not increase the quantity.

TABLE V. PHOSPHATE FOUND

Weight of Sample Gram	Aliquot	Weight of Precipitate Gram	P ₂ O ₅ %
0.0249	1	0.2269	31.60
0.1387	0.5	0.6287	31.44
0.1587	0.5	0.7221	31.56
0.0373	1	0.3363	31.27
0.0351	1	0.3210	31.71
			Av. 31.51

Chloropentammine-cobaltichloride was found to be the most suitable ammine for the precipitation of germanates. Partial analysis of the compound indicated its formula to be $[\text{Co}(\text{NH}_3)_5\text{Cl}]_2\text{H}_4\text{Ge}(\text{Mo}_2\text{O}_7)_6$. Since some of the results were satisfactory, a variety of conditions was tried in an attempt to learn what factor in the precipitation was responsible for the uncertain values often obtained. Experiments were performed in which (1) the quantity of molybdenum oxide was decreased to just a trifle over the theoretical amount and the acid concentration was reduced to a point at which the ammine molybdate just stayed in solution, (2) the temperature of precipitation and the time of digestion at this temperature were carefully controlled, (3) the temperature to which the solution was cooled before filtering was controlled, (4) the time of standing before filtration was varied, and (5) precipitation was made in a cold solution with shaking. None of these variations led to consistent results; duplicate samples sometimes differed 10 to 50 per cent.

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Fluorescent Light Microscopy

Possible New Applications to Industrial Research

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THE application of fluorescence—that is, visible light emanated by a substance which is being irradiated with invisible ultraviolet light—in microscopy is not of recent date. However, the development has been slow, mainly because of the technical difficulty of obtaining sufficiently concentrated light of high intensity in the ultraviolet spectrum. Only comparatively recently has it been possible to devise such light sources.

Haitinger's (2) great contribution to the final improvement of the light source, as the result of a systematic spectrographic search, was the introduction of iron electrodes that give an extremely efficient radiation between 3000 and 4000 Å. These electrodes are held in specially constructed brackets, guaranteeing effective cooling. They are bored vertically, to enable filling this channel with a substance that prevents excessive oxide formation, so that the arc can be easily started. This feature also assists materially in obtaining a very stable quiet arc. In collaboration with the firm C. Reichert, this new light source has been optically perfected, so that we have at our disposal today in the "Kam F" (Reichert catalog Kam, List 6094e) high-efficiency equipment for fluorescence microscopy which has already proved its value, notably in botany and biology. The voluminous literature concerned with microscopical ultraviolet studies in general fields, the textile and paper industries, dyestuffs, tanning agents, resins, rubber, pearls, botany, biology, and analytical chemistry, indicates the importance of such investigations, but, in the authors' opinion, the ultraviolet microscope has not yet received the attention it so richly deserves, because its application to the study of industrial and theoretical physical phenomena has so far been neglected.

The authors therefore decided to determine in a series of preliminary studies some possible uses of this instrument in industrial and theoretical physical research. The studies were carried out in a very general manner in order to determine as many applications as possible and the findings reported here are therefore only of a broad introductory nature. However, it is hoped that they may form the basis of further and more intensive research along the lines indicated, or sug-

gest other possible uses for the fluorescent light microscope that have not yet been considered.

Emulsification

The phenomenon of emulsification depends essentially upon the dispersion of one immiscible liquid in another. Consideration of the theories of emulsification and modern methods used in the preparation and study of these systems (1) led to the belief that visual observations of emulsification might be made with the fluorescent light microscope.

The first essential in any study with the fluorescent light microscope is to obtain materials which are visible in the field of the instrument, because of the natural fluorescent characteristics of the components present or the addition of small amounts of adsorbable fluorescent substances, so-called "fluorochromes." It is also most valuable in studying a system of two or more components to obtain as many fluorescent color differences in the excited visible light as there are constituents in the system, unless these can be clearly identified by structural or other properties. Since a two-component system is the simplest type of emulsion possible, it was deemed advisable to begin with the study of an emulsion of water and a neutral oil. Pure water is known to be nonfluorescing, so that it remained to select an oil which would exhibit suitable fluorescence. A purified paraffin oil exhibits a very faint blue fluorescence which was not considered sufficiently pronounced for the studies in mind. There are other oils which exhibit very pronounced fluorescence, but when an inactive hydrocarbon, such as anthracene, is dissolved in paraffin oil it becomes very strongly fluorescent in the deep blue.

When a drop of water is brought in contact with a drop of anthracene-treated paraffin oil on a u. v. transmitting slide and the system is immediately observed with the ultraviolet light microscope, using transmitted light, only the drop of blue fluorescing oil is visible in the field. [The magnification throughout these studies was maintained at 99 diameters (11× objective, 9× ocular) since this was found to give the best resolution of the phases in the systems considered.] As the time of observation increases, tiny crystals exhibiting

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a light greenish blue fluorescence are seen to form in the oil drop close to the interface. The crystals, in a fairly wide band extending from the oil-water interface into the main body of the oil drop, are in constant directional motion almost parallel to the interface but gradually moving to the oil side of the oil-water interface, where they aggregate in clusters with con-

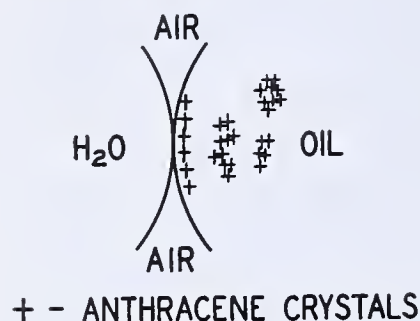


FIGURE 1

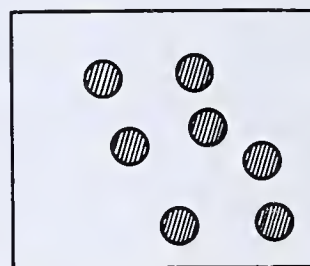
tinued but noticeably slower motion along the interface (Figure 1). No motion or orientation of the crystals is noticeable in the remainder of the oil drop. Still another interesting effect can be seen along the oil side of the oil-water interface extending for a comparatively short distance from the oil-water-air interface,

where not only is no crystallization visible but also no tendency for crystal movement into these regions. The above admittedly preliminary experiment indicates visually the movement of crystals in an oil-water interface and no doubt analogous effects take place when solids are used in emulsification processes. The crystals might thus be compared to solid emulsifiers and it might be inferred from these observations that the stabilization of an emulsion with a solid depends upon the formation of a protective film of the solid at the interface in the phase which wets the solid most readily. The latter suggestion was not investigated in detail in the present survey, but it is felt that a complete investigation of emulsification with solids offers a very fertile field of research with the fluorescent microscope.

It has long been known that ultraviolet light promotes crystal growth from solution, although the possibilities of this phenomenon have not as yet been sufficiently considered. The anthracene crystallization from the paraffin oil evidently took place from a solution which was not supersaturated with anthracene, since it was ascertained that this crystallization takes place in the absence of water, and continued irradiation of an oil drop with ultraviolet markedly decreases the intensity of the original blue fluorescence of the oil solution. This crystallization effect would indicate that the solubility of anthracene in paraffin oil is decidedly less in ultraviolet than in visible light. However, it has been shown (6) that anthracene is converted into dianthracene, a less soluble form, when irradiated with ultraviolet, the amount of the conversion being proportional to the amount of energy absorbed. This conversion effect is true for other organic compounds, but it is also stated (6) that dianthracene is not fluorescent, whereas the crystals referred to above exhibited a decided greenish blue fluorescence. This would indicate either that these crystals are not dianthracene, or that anthracene is adsorbed on the dianthracene crystals, causing them to fluoresce, or contrary to the former statement, that dianthracene is naturally fluorescent. Further study is necessary to decide the issue, but it would seem that ultraviolet light might be advantageously applied in crystal-purification methods in spite of the possible formation of polymers, since these are generally reversible and are usually easily reconverted to the original compound.

A solution of rosin in an asphalt-base crude oil fluoresces a greenish blue in the ultraviolet and remains stable with time. If a drop of water is brought in contact with a drop of this oil and the system is observed with transmitted ultraviolet light in the microscope, no change is noticeable at the oil-water interface. Upon stirring a small amount of oil into the water drop in the field of the instrument, greenish blue

droplets of oil are seen to be dispersed in the water and it is particularly noticeable that these droplets are homogeneous in color structure. When a drop of 1 per cent solution of sodium hydroxide instead of water is brought in contact with a drop of oil containing rosin, a beautiful blue fluorescent band is visible at the interface between the two liquids. This band is no doubt due to the formation of sodium resinate, which being capillary-active is adsorbed at the interface, exhibiting its characteristic blue fluorescence. The effect of this adsorption is more strikingly demonstrated when the two drops are stirred together, for each droplet is observed to be surrounded with a strongly fluorescent blue ring (Figure 2). It should be pointed out that the visibility of this band is dependent upon the size of the droplets, because it is evident that this adsorption effect must take place around the entire drop and is visible as a ring only because of the thickness of the droplets. This is readily demonstrated with incident light, for the oil droplets in pure water remain as before a greenish blue, whereas those in sodium hydroxide solution exhibit a deep blue fluorescent color throughout.



////- GREENISH-BLUE
-- BRIGHT BLUE

FIGURE 2

observed in the ultraviolet microscope. A beautiful band of blue fluorescence is again noticeable at the oil-water interface. When the two drops are mixed in the field of the instrument, a rather unstable dispersion is formed, but in this case the blue rings are not visible around the dispersed phase. This is to be expected, since the continuous phase is now oil which fluoresces a bluish green and hence obscures the blue color of the calcium resinate adsorbed on the surface of the water droplets.



FIGURE 3

This study with the two types of emulsions suggested the possibility of using the fluorescent microscope to determine the dispersing phase in an emulsion. When a crystal of anthracene, which is oil-soluble, is added to the above emulsion prepared with calcium chloride, a blue fluorescent halo develops around the crystal and gradually spreads through the system. This demonstrates that the emulsion prepared with calcium chloride is of the water-in-oil type. If the same procedure is now repeated with the sodium hydroxide emulsion as used above, no halo is formed around the anthracene crystal, indicating that the dispersing phase in this case is water and the emulsion is of the oil-in-water type (Figure 3).

Ore Flotation

The concentration of ores by flotation depends essentially upon the preferential surface conditioning of minerals to cause

them to become attached to air bubbles and thus be floated, whereas the accompanying gangue or tailing, being unaffected by the treatment, remains in equilibrium with the water phase and hence sinks. The principles of ore flotation as they have been suggested by both practical application and theoretical research have been adequately considered in the literature (5), but the nature of the mechanism of this action is for the most part still very indefinite. Actually following the process of ore flotation by some visual method would therefore seem extremely important. This suggests the use of the fluorescent light microscope if one could distinguish differential fluorescence in the systems studied. The particular system considered in this article, the flotation of galena from sand with oleic acid and amyl alcohol, is only one of a great many possible systems, but it demonstrates the value of the ultraviolet light microscope in such studies.

When a mixture of galena, sand, amyl alcohol, oleic acid, and water is shaken in a test tube and the tube is held in the path of ultraviolet light, it is immediately evident that the foam on the surface is very strongly fluorescent in blue, while the main body of the liquid is much less so. This effect is more marked at fairly low concentrations of oleic acid and amyl alcohol if the proportions of the solid constituents in the system are kept relatively constant. Since the foam, according to suggested theories, contains the galena ore as well as the greater portion of the oleic acid and amyl alcohol, a study of the ore-flotation process with the fluorescent light microscope seems feasible.

In actual ore-flotation processes the efficiency of the ore separation is dependent in part upon the size of the solid particles in the system. A few tentative experiments were therefore made to determine the most suitable particle size for the studies in mind. Solid particles of sand and galena passing through a 20-mesh but retained by a 48-mesh screen seemed to be best.

Galena ore observed in the fluorescent light microscope does not fluoresce with transmitted ultraviolet light, although a very faint reddish fluorescence is noticeable with incident light, and the wetting of the galena particles with water produces no visible alteration in the ultraviolet. When particles of galena are shaken with water having a drop of oleic acid floating on its surface, the excess solution is decanted off, and the wetted particles are observed in the fluorescent light microscope with transmitted ultraviolet light, all the galena particles are seen to be surrounded with a definite layer of greenish blue fluorescent material, characteristic of oleic acid, whereas with incident light only homogeneous greenish blue particles are visible. It is obvious that the whole surface of the galena particles must be coated with oleic acid, obscuring the particle with incident light but indicating it as a black body with transmitted light.

Transmitted light, therefore, serves to indicate a cross section of the adsorbed materials surrounding the mineral, and being therefore much better suited to the observation of the details to be studied was used through the remainder of this study. When a drop of amyl alcohol is brought in contact with the above wet agglomerate of galena while the layer of oleic acid and the dark wall of one of the galena particles are in constant observation, an explosive reaction occurs—i. e., the layer of oleic acid is rapidly made more diffuse and tiny galena particles are observed to have broken off the wall of the galena crystal. The latter phenomenon is thought to be due to cracks or capillaries in the surface structure of the ore, and the spreading of the oleic acid by the amyl alcohol is so violent and rapid in action that the outside edges of the mineral are shattered by the forces exerted in these hypothetical crevices. There is also the possibility that galena may be made up of a plate or disk-like lattice or units analogous to the structure of "Dickite," a kaolinite clay mined in Colorado.

If galena particles are first shaken with water and amyl alcohol and the excess solution is decanted, the particles are observed to be surrounded with a very diffuse halo of blue fluorescence, the intensity of which is dependent upon the concentration of amyl alcohol originally used. When a drop of oleic acid is brought in contact with this wet mass, observation of the edge and surrounding of one of the galena particles shows that the drop passes to the surface of the mineral as a diffuse layer without any bursting of the galena particles. This is shown not only by the actual motion of the oleic acid but also by the decided increase in fluorescence surrounding the particles and a change to a greenish blue.

When sand is observed in the ultraviolet, only a very few particles are noticeably fluorescent in the yellow and red, probably because of some impurity, and no visible alteration of the particles occurs with the addition of water. If a few particles of sand are shaken in a test tube containing water and oleic acid and these wetted particles are observed in the fluorescent light microscope, very few of them exhibit the greenish blue fluorescence of oleic acid around their edges, and in the cases where this is true the bands of fluorescence do not always surround the mineral but are in some cases confined to only one edge or spots. The latter effect is probably due to the presence of mineral impurities preferentially wettable by oleic acid in the sand particles which might conceivably be present in only localized areas of the sand. A drop of amyl alcohol added to this agglomerated mass causes some agitation and pushing apart of the sand particles, while the blue fluorescence of the alcohol becomes evident throughout the system.

These experiments in the study of ore flotation with the fluorescent light microscope have so far considered each solid component in a separate system. It now remains to study sand and galena in a single system.

When galena, sand, water, and oleic acid are shaken together and the wetted solids are observed with the fluorescent microscope, it is noted that many particles are coated with a layer exhibiting a greenish blue fluorescence, whereas the remaining particles do not show this effect. The particles exhibiting the band of fluorescence are readily identified as galena because of their characteristic cubical shape (Figure 4). The addition of amyl alcohol to the system has the same explosive effect on the galena as previously described. Sodium *n*-amyl xanthate, a collecting agent commonly used in ore-flotation practice, when used in conjunction with oleic acid does not differ appreciably from amyl alcohol in its effect and therefore needs no further discussion here.



FIGURE 4

General Studies

The experiments discussed above have been confined to specific practical problems and their study with the fluorescent light microscope, but during these experiments certain other possible uses of the fluorescent light microscope were suggested.

One of the most difficult problems in the study of wood structure by microscopical methods is the preparation of microtome sections for use with transmitted light. This is especially true in a study of wood in a partially destroyed state, such as that resulting from advanced decay. The Leitz Company was the first to offer a solution for this problem

by introducing the "Ultropak," which does not require thin sectioning since it employs incident light. As the studies considered here are not concerned with visible light, the discussion will be limited to observations with the fluorescent light microscope.

When a block of poplar wood is observed under the fluorescent light microscope with incident light, which does not require microtome sections, it exhibits the characteristic light-blue fluorescence common to wood. Although the structural details of the wood are extremely clear, no differential fluorescence in the structure is indicated. Koehler's (4) suggestion of the use of "colorless dyes" in fluorescent light studies prompted a study of their use in determining the different structural components known to be present in wood. When sections of poplar are submerged in various fluorescent dyes and are then observed under the ultraviolet microscope in their wet state, only the primulin dye (a yellow cotton dye obtained by heating paratoluidine with sulfur and then sulfonating the reaction product) shows preferential adsorption on the wood section. This is evidenced by distinct differential color fluorescence in pink, blue, and green. These



/// - AREA PENETRATED
AS SHOWN BY
FLUORESCENCE OF
PENETRATING SOLUTION

FIGURE 5

fluorescent colors are not dispersed on the wood in a heterogeneous manner, but are homogeneously dispersed on definite structural elements of the wood. The selectivity of the primulin is not altered with drying the wood section.

In the course of the above studies with wet wood sections, the clearness of the liquid menisci in various pores was particularly noticeable. This suggested the possibility of studying the rate of penetration of liquids into these surface pores. A drop of anthracene-treated oil was brought in contact with the outer surface of a wood block and the movement of the menisci observed under the fluorescent light microscope. Most of the menisci moved through the field rapidly, only a few moving slowly enough to be readily followed. A complete study would therefore require the selection of a suitably viscous oil or fluid. In any case the anthracene-treated oil upon filling the pores produced a beautiful picture of the capillary structure of the wood surface, for the pores fluoresced bright blue whereas the capillary walls remained greenish blue.

One of the most difficult problems in the study of commercial impregnation of porous materials with liquids is the determination of the depth of penetration when the penetrating substances are colorless or their color is obscured by the solid. The fluorescent light microscope offers a solution to this problem, for the depth of penetration is shown either by the natural fluorescence of the penetrating liquids themselves or by that of small amounts of fluorochromes added to the liquids before impregnation. The latter is better than the use of colored dyes, because visible color is undesirable in most finished products where colorless liquids have been used for impregnation. The use of the fluorescent light microscope for determining the depth of penetration has already found an application in the leather industry (determination of depth of tanning) and it is hoped that it will prove valuable in other industries concerned with impregnation processes (Figure 5).

Another possible use is in the identification of molds and fungi, of extreme importance in many industrial and scientific fields. This may be based on either natural or incited differences in fluorescence among the organisms. A few wood-destroying fungi were observed with ultraviolet light and

exhibited natural greenish blue fluorescence in all cases except one, where pinkish fluorescence was noticeable. A number of other uses of the fluorescent microscope have come to mind through this series of studies, but it seems rather futile to attempt a discussion of them without first tentatively verifying their possibilities.

Although some of the suggested applications may prove of little value, the authors are confident that others will be most valuable in broadening our knowledge of the mechanism of processes to be investigated. In publishing this admittedly very superficial general survey at this time the authors hope to incite others to make increasing use of this new experimental tool in research activities that have heretofore evaded visual observation. Theoretical details and the application of fluorescent light microscopy in the study of adsorption and other surface phenomena are presented in another article (3).

Summary

Since the construction of highly efficient and highly concentrated ultraviolet light sources, fluorescent light microscopy has proved of constantly increasing interest and value in a great number of applications—for example, in biological and botanical research, in inorganic analytical chemistry, as a routine control method in the textile and paper industries, etc. However, fluorescent light microscopy lends itself perfectly to the study of typical colloid physical or chemical processes or reactions, and permits for the first time visually demonstrating and following such processes as the production and destruction of emulsions, and the influence of different types of emulsifying agents on the stability of the system. It offers a simple, quick, and reliable method of determining types of emulsions which so far have been difficult to ascertain.

Fluorescent light microscopy promises to become a valuable new method in detailed studies and routine control of flotation processes. It is applicable in studying the degree of penetration into porous absorbent matter—for example, in the tanning of leather with different types of natural or synthetic tanning agents. This new technic is of value in the study of wood preservation and in the detection of molds or fungi.

Since modern fluorescent light microscopy permits the use of incident as well as transmitted light, it becomes unnecessary to prepare microtome sections and to apply selective dyeing methods.

The use of "colorless" dyes of high fluorescing power further broadens the applicability of this method in cases where the substance itself does not emanate fluorescent light if radiated with invisible ultraviolet light.

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RECEIVED September 18, 1936.



Organic Microanalysis

II. Drying and Analysis of Hygroscopic Substances

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HYGROSCOPICITY is especially important to the microanalyst where the small size of sample and relatively large area exposed may lead to difficulties that vanish when working on a larger scale. The methods of Pregl (5) are in general probably satisfactory for drying substances which only adsorb water on their surface. In localities where the temperature and relative humidity are low throughout the year such materials should give little trouble. The case is quite different with compounds which form hydrates or solvates and those, such as proteins and nucleic acids, where a large molecule of great surface area, usually noncrystalline, is present without very definite composition. As a typical example, 3 mg. of a substance with a molecular weight of 480 can form its monohydrate with the amount of water contained in 5 ml. of air (partial pressure of water 22.0 mm.). Even though the drying has been successful in Pregl's microdesiccator or other apparatus, the time of exposure in removing it to the "pig" for weighing and introducing it into the combustion tube may be sufficient for it to hydrate completely.

The apparatus and procedure described below for handling compounds tending to absorb water rapidly upon the unavoidable exposure to atmospheric moisture during analytical manipulations are an improvement over the old type of Abderhalden drier, in that the pig containing the dried sample can be closed inside the apparatus. The importance of this point is discussed more fully by Booth and McIntyre (1) as it affects desiccators.

Advantages of this apparatus are well illustrated by the authors' experience in analyzing chrysanthemin chloride and its derivatives (6). This substance was not hygroscopic as received for analysis and lost little or no weight upon drying in the old type of Abderhalden at temperatures up to 140° C.

The analyses were always low in carbon and high in hydrogen even on drying at 140° C. and a pressure of less than 10^{-5} mm. of mercury, usually by amounts which showed the presence of from one to one and a half molecules of water per molecule of chloride. After the present apparatus was developed and the pig capped while in the drier, excellent analyses were secured on drying at 100°. Apparently chrysanthemin chloride is a compound forming a hydrate with a low partial pressure of water at room temperature. Experiment showed that the anhydrous form completely hydrates on exposure to the room air in as little as 10 seconds. The apparatus also proved of great value in studying the unusual water and alcohol solvates of 1-*d*-glucosidocytosine which were discussed by Hilbert and Jansen (4).

The details of the apparatus are shown in Figures 1 and 2.

A vapor bath maintains a constant temperature as in the ordinary Abderhalden. The two-way stopcock can be turned to permit evacuation or the drying of incoming air, the latter entering through a very fine capillary cemented in the plug of the cock and then through the U-tube containing the desiccant. Colored Anhydrite (anhydrous calcium sulfate) has proved very satisfactory as a drying agent. The other end of the tube carries two ground joints, a large one for introducing the plate holding the pig and a small one to hold the brass rod used to open and close the pig while the sample is in the drier. A closed-end mercury manometer is used to seal the small ground joint and to indicate leaks if present when the apparatus is evacuated overnight.

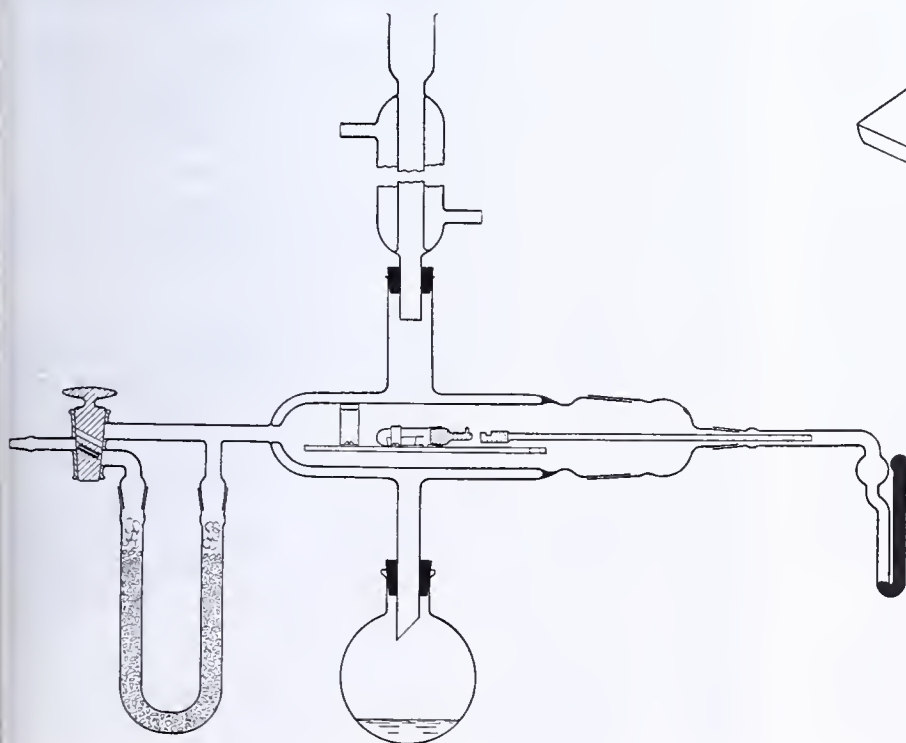


FIGURE 1. DRIER WITH PIG AND BOAT IN PLACE

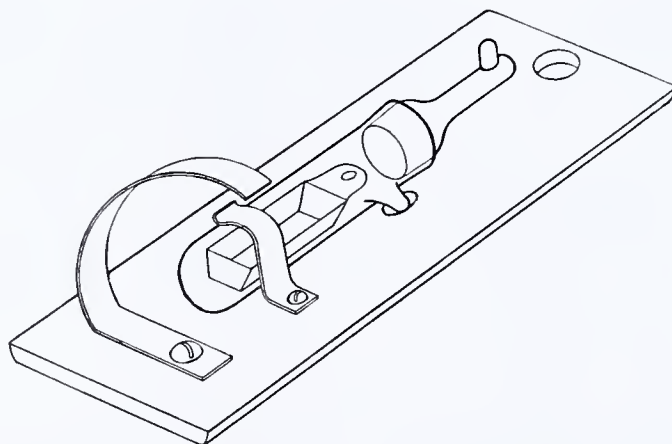


FIGURE 2. DETAIL OF PIG HELD ON BASE

The Pyrex pigs used are shorter than in the Pregl type and do not have the long handles recommended by Pregl (5). Stability is much greater without these handles, and with tweezers curved to fit the pig and chamois over the fingers the glass is not unduly heated by the hand and the pig is easily handled. No difficulty has been encountered in securing constant weights, although the glass is heavier and the pig more substantial than in the Pregl type. A phosphor-bronze spring clip holds the pig firmly in place on an aluminum base with two depressions for the front legs.

The pig is easily transported while on this plate. The base, whose edges are curved to fit the drier, is held fixed within the drier by another spring clip as shown in Figure 1. The solid glass stopper of the pig has a small handle with projecting knob which is engaged by a brass sleeve comprising a bayonet joint

and enables the stopper to be withdrawn or firmly seated while the pig is in the drier.

The effectiveness of this apparatus was tested on cupric sulfate pentahydrate. A few clear crystals were selected and crushed; 9.783 mg. weighed in a previously dried boat and pig were heated in the apparatus 0.5 hour at 100° C. and pumped during only half this time. The loss in weight was 3.102 mg., corresponding to 4.4 moles of water per mole of sulfate. This may have been all the water originally present in the sulfate; for the present purpose it does not matter. The efficiency of the apparatus and procedure is shown by the fact that two more treatments for the same time gave no further gain or loss, in spite of the fact that the vapor pressure of this substance is approximately 2.7 mm. (2) and the average room temperature was 26.67° C. (80° F.), with relative humidity of 65 to 80 per cent.

In the analysis of organic compounds the following procedure is used. It eliminates much of the work in the method proposed by Hayman (3). The method has been generally applied in this laboratory for the last several years in organic

microanalytical determinations on many hundreds of compounds.

Before the sample is weighed out, the pig and empty boat are dried and capped in the apparatus. The sample is weighed and dried and the result recorded. Then the pig is opened and the sample allowed to equilibrate with the moisture in the room. Usually after 30 to 60 minutes equilibrium is so nearly approached that any further gain in weight while transferring the sample to the combustion tube is negligible. The pig is then closed and reweighed. The gain in weight upon exposure to air is subtracted from the weight of water found before the percentage of hydrogen is calculated.

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Microscopical Qualitative Analysis of Antimony and Bismuth

Tetraethyl Ammonium Iodide as a Reagent

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OF THE existing microscopical tests for antimony and bismuth, none is sufficiently free from interferences to be satisfactory. Since these two elements often occur together, especially in alloy samples, it is desirable that characteristic reactions should be developed rather than that separation methods should be elaborated, for in rapid analysis a series of preliminary treatments or the precise control of conditions is usually impractical.

A brief review (1) of the best microscopical reactions for antimony and bismuth is in order, since in an analysis it is often desirable to employ several tests as checks, or conditions may necessitate the use of one which is not of the highest sensitivity.

Cesium chloride gives double salts, $3\text{CsCl} \cdot 2\text{SbCl}_3$, colorless hexagonal plates or rosettes, and $3\text{CsCl} \cdot \text{BiCl}_3$, colorless rhomb-shaped plates, with pure salts. However, $3\text{CsCl} \cdot 2\text{BiCl}_3$, isomorphous with the antimony double salt, will form if cesium chloride is not in excess, or if antimony is present. Ag, Pb, Hg^+ , Cd, Sn, Tl^+ , and Cu may also yield crystalline precipitates of distinctive appearance, but in complicated mixtures or for the detection of relatively small amounts of the elements sought cesium chloride is not specific or sensitive enough.

Cesium sulfate yields, with bismuth as sulfate, hexagonal plates; no reaction is given with antimony. Sodium sulfate gives rods or short prismatic crystals. Insoluble sulfates and alum-forming elements interfere.

Potassium binoxalate gives tiny tetragonal "octahedra" with bismuth, and trichites with antimony, but so many other metals yield insoluble oxalates that this reaction is useful only for relatively pure salts.

Antimonyl tartrates of potassium or barium, possessing characteristic crystal forms, are subject to this same objection.

Stibine, generated on a micro scale, may be used as a means of identifying antimony, since bismuth forms no analogous hydride.

Metallic bismuth, obtained by the reduction of bismuth salts by sodium stannite, is useful confirmatory evidence, since antimony is not reduced under similar treatment.

Bismuth cobalticyanide gives a crystalline precipitate, but is not suitable for mixtures containing much antimony. Numerous organic reagents (alkaloids, etc.) have been suggested, most of which yield "amorphous" precipitates, and are subject to interferences.

Reactions with Tetraethylammonium Iodide

When a solid fragment of tetraethylammonium chloride is added to a fairly concentrated hydrochloric acid solution of antimony trichloride, colorless hexagonal plates or short prisms are formed. If an excess of potassium bromide is present, colorless hexagonal plates and tablets or short hexagonal prisms will be formed. Both compounds are fairly soluble, and no precipitate will be obtained from dilute solutions of antimony. Both compounds give a positive, uniaxial interference figure.

Pentavalent antimony yields a colored and much less soluble precipitate of purple hexagonal plates (Figure 1, left) if iodides are present in a test drop containing even a very dilute solution of antimony. When the concentration of antimony is high, the crystals are likely to be imperfect (fragments, ribbed plates, skeletal stars), and so thick as to appear black. Attempts to prepare this compound in sufficient quantity for analysis failed because of its instability. It may be analogous to the bromo compound reported by Petzold (5) which forms "red pyramids" of the formula $[(\text{C}_2\text{H}_5)_4\text{N}][\text{SbBr}_6]$.

Trivalent antimony gives yellow anisotropic crystals which are usually too small to be reliable as an identifying form. These crystals generally appear in clusters of three or four, but some individuals may become large enough to be identi-

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fiable as rhombohedra growing on a pinacoid face. In concentrated solutions many trigonal and hexagonal plates and also a few hexagonal prisms may grow.

In nearly all cases some purple hexagonal plates of the pentavalent antimony compound will appear with the yellow crystals from trivalent antimony, either immediately or near the edges as the drop evaporates. If the test drop is allowed to stand in the air for 4 or 5 minutes before making the test, the hexagonal plates will appear in large numbers, indicating that antimony is oxidized by free oxygen.

Attempts to analyze the yellow compound formed by trivalent antimony have been unsuccessful because it decomposes on standing.

Trivalent bismuth precipitates as small dark amber triangular plates, tablets, or clusters of the same habit as those given by trivalent antimony, but generally larger (Figure 1, right). When mixtures of trivalent antimony and bismuth are precipitated, the color of the crystals obtained varies from yellow to dark amber as the proportion of bismuth is increased, and there is only one crystal habit. This is evidence that the antimony and bismuth compounds are isomorphous.

Because of this isomorphism, trivalent bismuth might be interpreted as antimony or vice versa. Oxidation can be utilized to accentuate the difference between these elements, for antimony can readily be rendered pentavalent by evaporation to dryness with nitric acid, while bismuth is not easily oxidized under similar conditions. The purple hexagonal plates of tetraethylammonium antimony iodide then constitute a distinctive test for antimony, and cannot be confused with the amber rhombohedral grains due to bismuth.

TABLE I. SENSITIVITY OF THE (C₂H₅)₄NI TEST FOR ANTIMONY IN THE PRESENCE OF INTERFERENCES^a

Interference, <i>M</i>	Direct Test		Volatilization in Presence of SnCl ₂	
	Ratio Sb/ <i>M</i>	Smallest quantity detectable, Sb ⁺⁵	Ratio Sb/ <i>M</i>	Smallest quantity detectable, Sb ⁺⁵
	%	Gram	%	Gram
Bismuth	1.0	3. × 10 ⁻⁶	0.04	0.2 × 10 ⁻⁶
Cadmium	0.05	0.2 × 10 ⁻⁶
Copper (ous)	1.0	1.5 × 10 ⁻⁶	0.03	0.2 × 10 ⁻⁶
Lead	3.0	25.0 × 10 ⁻⁶	0.05	0.4 × 10 ⁻⁶
Mercury	2.0	20.0 × 10 ⁻⁶	0.05	0.4 × 10 ⁻⁶
Tin (ous)	0.2	3.0 × 10 ⁻⁶	0.02	0.2 × 10 ⁻⁶
Tin (ic)	0.02	0.2 × 10 ⁻⁶	0.02	0.2 × 10 ⁻⁶
Oxidizing agents:				
Arsenic (AsO ₃ ⁻³)	4.0	25.0 × 10 ⁻⁶	0.03	0.2 × 10 ⁻⁶
Arsenic (AsO ₄ ⁻³)	7.0	25.0 × 10 ⁻⁶	0.03	0.2 × 10 ⁻⁶
Copper (ic)	1.0	1.5 × 10 ⁻⁶	0.03	0.2 × 10 ⁻⁶
Iron (ic)	1.0	1.0 × 10 ⁻⁶	0.07	0.2 × 10 ⁻⁶

^a In the absence of interferences the sensitivity is: concentration limit, 2 × 10⁻⁶ gram of Sb⁺⁵ per cc. or 1 to 500,000. Smallest quantity detectable, 0.05 × 10⁻⁶ gram of Sb⁺⁵.

Bismuth alone, after the above treatment, may yield with the reagent a few light red to pale pink very thin hexagonal plates along with the amber grains. These are evidently isomorphous with the purple hexagonal plates from pentavalent antimony for, when a solution of the latter is added to a test drop containing them, they become much darker and more purplish. Also, when crystals prepared by precipitating the pentavalent antimony compound in the presence of bismuth are treated with sodium stannite, they are blackened, owing to the bismuth in solid solution, whereas if antimony alone is present the crystals are completely dissolved. However, it is apparently not possible to complete the oxidation to pentavalent bismuth by the use of nitric acid and the amber grains are the chief constituent of the precipitate.

The pentavalent antimony tetraethylammonium iodide is apparently not isomorphous with the well-known isomorphous

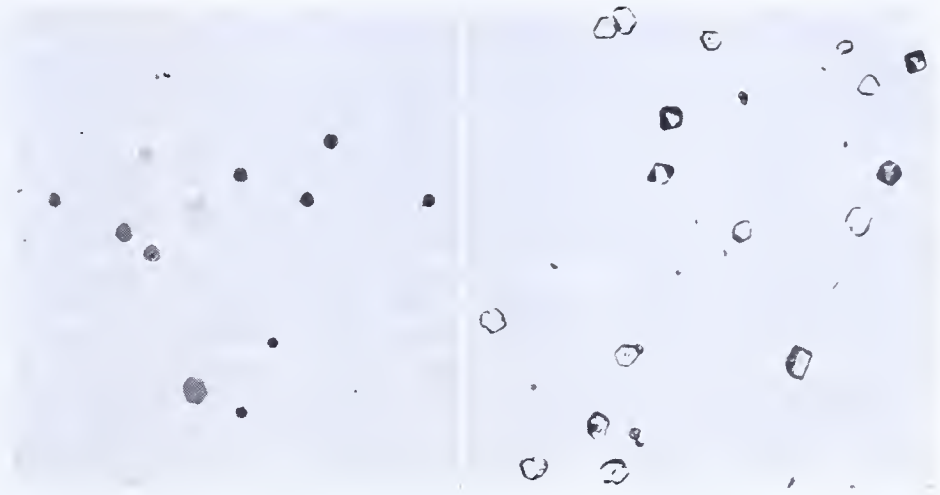


FIGURE 1. CRYSTALS OF ANTIMONY AND BISMUTH

Left, Sb⁺⁵ with (C₂H₅)₄NI. 100 ×
Right, Bi⁺³ with (C₂H₅)₄NI. Sb⁺³ gives similar crystals. 100 ×

compounds, 3CsI·2BiI₃ and 3CsI·2SbCl₃, which form orange-red hexagonal plates. Numerous substituted ammonium complexes with antimony and bismuth are described in the literature (3, 4, 6, 7). It seems probable that the formula of the precipitate with trivalent antimony or bismuth is 3(C₂H₅)₄NI·2SbI₃ or 3(C₂H₅)₄NI·2BiI₃, and that pentavalent antimony yields (C₂H₅)₄NI·SbI₅.

TABLE II. SENSITIVITY OF (C₂H₅)₄NI TEST FOR BISMUTH IN THE PRESENCE OF INTERFERENCES^a

Interference, <i>M</i>	Direct Test		NaSnO ₂ on Dry Residue after Pptn. by (C ₂ H ₅) ₄ NI Plus KI	
	Ratio Bi/ <i>M</i>	Smallest quantity detectable, Bi ⁺³	Ratio Bi/ <i>M</i>	Smallest quantity detectable, Bi ⁺³
	%	Gram	%	Gram
Antimony	10	25 × 10 ⁻⁶	0.08	0.2 × 10 ⁻⁶
Cadmium	0.05	0.2 × 10 ⁻⁶
Copper (ous)	1.0	1.5 × 10 ⁻⁶
Lead	3.0	25.0 × 10 ⁻⁶	0.05	0.2 × 10 ⁻⁶
Mercury	1.7	12.0 × 10 ⁻⁶	0.05	0.2 × 10 ⁻⁶
Tin (ous)	1.0	12.0 × 10 ⁻⁶
Tin (ic)	0.02	0.2 × 10 ⁻⁶
Oxidizing agents:				
Arsenic (AsO ₄ ⁻³)	2.0	6.0 × 10 ⁻⁶	0.1	0.2 × 10 ⁻⁶
Arsenic (AsO ₃ ⁻³)	1.0	6.0 × 10 ⁻⁶	0.1	0.1 × 10 ⁻⁶
Copper (ic)	1.0	1.5 × 10 ⁻⁶
Iron (ic)	2.0	3.0 × 10 ⁻⁶
With K ₂ SO ₃ (ous)	0.1	0.2 × 10 ⁻⁶

^a In the absence of interferences the sensitivity is: concentration limit, 2 × 10⁻⁶ gram of Bi per cc. or 1 to 500,000. Smallest quantity detectable, 0.05 × 10⁻⁶ gram of Bi.

^b Removal of mercury with SnCl₂, and oxidation of excess of SnCl₂ to SnCl₄ with HNO₃ before testing.

The acidity of the solution to be tested need not be controlled precisely; it is necessary to have enough hydrochloric acid present to prevent hydrolysis, but excess acid tends to dissolve the precipitates and lower the sensitivity of the test. It is possible to recrystallize the precipitates by warming with hydrochloric acid and allowing to cool; this yields larger crystals and may improve the sensitivity of the test when interfering substances are present.

Oxidizing agents, including cupric, ferric, and arsenate ions, interfere by liberating iodine, which may give yellow crystals with tetraethylammonium chloride, or may appear as black to brown rhombs and prisms of the element. Potassium sulfite will reduce the free iodine without reducing the antimony or bismuth, unless the solution is heated.

Mixtures and Possible Interferences

Antimony in the presence of bismuth will be recognized most readily by the purple plates of the Sb⁺⁵ compound, after oxidation with nitric acid but, since bismuth may in dilute solutions yield some red to pink hexagonal plates, the distinction is not conclusive if the ratio of antimony to bismuth is less than about 1 per cent.

The volatility of antimony trichloride (b. p. 220°) may be utilized to separate it from interfering substances, with a corresponding increase in the sensitivity of the reaction. The acidified test drop is heated nearly to boiling above a microburner, while just above its surface a slide carrying a small hanging drop of tetraethylammonium chloride solution is held. The upper slide is cooled, a drop of water is added to the reagent, and then a fragment of potassium iodide is introduced into this solution. As the drop concentrates by evaporation, crystals of the antimony compound will form. (Crystals of a compound between the reagent and potassium iodide may appear next to the potassium iodide fragment, but these are easily disregarded.)

The separation just described is most satisfactory if a drop of stannous chloride has been added to the unknown just before volatilization. Stannous chloride reduces the oxidizing agents, acts as a carrier for antimony, and provides an acid atmosphere. The amount of tin carried over does not reduce the sensitivity of the test.

Arsenic in the form of arsenites or as As^{+3} will give large, yellow, hexagonal or trigonal plates of arsenic triiodide when potassium iodide is added to the test drop, but this compound is too soluble to cause trouble unless the concentration of arsenic is high, and its formation can be avoided by diluting the test drop. Addition of the reagent then causes no change. The chief difficulty is caused by the fact that arsenites are readily oxidized by the air to arsenates which liberate iodine. The limit of sensitivity in the presence of arsenates is 4 per cent of antimony, or 2 per cent of bismuth. If potassium sulfite is used to minimize the liberation of iodine, the limit of sensitivity can be somewhat extended.

The use of stannous chloride and separation by volatilization of antimony trichloride is desirable in the presence of arsenic. The limit of sensitivity is 0.03 per cent of antimony.

The use of stannite solution as described below permits a limiting ratio of 0.1 per cent of bismuth to arsenic.

Bismuth in the presence of antimony is not recognizable with absolute reliability by means of tetraethylammonium iodide. The most useful confirmatory reaction is based upon reduction to metallic bismuth by stannite solutions. If there is any question as to whether the colored (pink to purple) hexagonal plates obtained after oxidation and treatment with tetraethylammonium chloride and potassium iodide are the bismuth compound, or contain bismuth in isomorphous mixture with the antimony compound, flooding the dry residue from the test made in the usual way with a moderately concentrated solution of sodium or potassium stannite will result in a blackening of crystals containing bismuth. Pseudomorphs are formed if the ratio of bismuth to antimony is greater than 2 per cent; below this concentration black grains and skeletal masses of bismuth are formed (examine by reflected light and at high magnification, to be sure this residue is black). Crystals which do not contain bismuth will become white from the formation of hydrated antimony trioxide, and slowly dissolve. Trivalent antimony may be recognized in this solution, as yellow rhombohedral grains, by acidification with hydrochloric acid.

The stannite solution must be clean, and contain no black specks of tin. The reduction of the bismuth may not be immediate, and tin may separate in the crust at the edges of the test drop.

Lead compounds also may be reduced and blackened by the stannite reagent, but this occurs slowly in the cold. A very small amount of bismuth catalyzes the reduction (2) and may thus be recognized in smaller quantity than if lead were absent.

Cadmium may yield colorless rectangular plates, not to be confused with bismuth or antimony compounds.

Copper liberates iodine and forms fine granular (actually

isotropic tetrahedra) white cuprous iodide, soluble in excess of potassium iodide.

Iron (ferric) liberates iodine. If reduced by sulfite, there is no interference.

Lead is not completely precipitated as the chloride; the characteristic yellow hexagonal plates of its iodide are soluble in excess potassium iodide. When tetraethylammonium chloride is added to the solution containing Pb^{++} and potassium iodide, a precipitate of colorless needles and prisms may be formed; lead iodide is also likely to appear. Neither of these should be confused with the antimony or bismuth reactions. In the presence of much lead the crystals of the bismuth compound tend to become imperfect and leafy; tiny black needles are also likely to appear; the red bismuth compound may overgrow the edges of the plates of lead iodide. The ratio of antimony or bismuth to lead must be above 3 per cent for a positive test.

The stannite reduction affords an excellent means of avoiding the interference of lead with bismuth, but since the presence of bismuth will hasten the reduction (ordinarily very slow) of lead to the metal, it is desirable to compare the test with a blank made on lead alone.

Mercuric ion yields red mercuric iodide, soluble in excess potassium iodide, from which solution the reagent may cause yellow tapering prismatic crystals to form. After reduction with stannous chloride, metallic mercury may be separated from the solution to be tested, by decantation or filtration, and the liquid then evaporated with nitric acid and tested with tetraethylammonium chloride and potassium iodide. The volatility of mercuric chloride interferes with the separation of antimony as antimony trichloride, unless any mercury present has first been reduced in this manner.

Tin (stannic) may yield large colorless octahedra of potassium chlorostannate if present in large amount, and a red crust may form at the edge of the drop on evaporation, but these crystals are readily soluble, and not to be confused with those from antimony or bismuth. Stannous ion gives a precipitate of colorless to pale yellow rods, needles, or hexagonal prisms, and also reduces antimony to the trivalent condition. Unless some reoxidation by the air occurs, the characteristic purple plates from pentavalent antimony, or the pink ones obtained from bismuth, will not be produced. The amber rhombohedral grains of the trivalent bismuth compound will still appear. The needles and prisms of the stannous compound are amber to brownish red in the presence of bismuth, and are pleochroic; this coloring is a useful indication of bismuth in very small proportion (< 0.1 per cent). The interference of stannous tin is readily eliminated by evaporation with nitric acid.

Analytical Procedure

If the unknown is a solution, evaporate to dryness with nitric acid; then dissolve in about 3 *N* hydrochloric acid (Ag , Hg^{+} , and Pb may precipitate); add a fragment of solid potassium iodide to the test drop (note any significant precipitate— Ag , Hg , Pb , Cu , Se , Te , I —or color in solution— Bi , Sb , As). Then add a small drop of a moderately concentrated solution of tetraethylammonium chloride. Examine, and note any subsequent precipitation. If the product is too fine-grained, recrystallize by adding a little hydrochloric acid, warming gently, and cooling.

If numerous purple hexagonal plates are formed, antimony is present; if only a few pink ones, together with yellow granules, bismuth may be present. Confirm antimony by volatilization as antimony trichloride in the presence of stannous chloride. Confirm bismuth by the stannite reaction on the precipitate with tetraethylammonium chloride.

If the unknown is a solid, dissolve in water if possible, noting any indications of hydrolysis to oxy compounds (Sb , Bi). Wash any residue, and extract with 3 *N* hydrochloric acid, or with aqua regia. Evaporate almost to dryness by warming gently, dissolve in 3 *N* hydrochloric acid, and test as above.

If the unknown is an alloy, treat with concentrated nitric acid in a microcrucible (note any formation of white oxides of tin or

antimony), and evaporate to a thick paste to remove excess acid. Extract the residue with water to remove soluble nitrates of possible interfering metals. Then extract the hydrolyzed residue of stannic oxide and oxynitrate of antimony and bismuth with warm 3 *N* hydrochloric acid, in which antimony and bismuth will be dissolved and can be tested for as above. If very small amounts of antimony and bismuth are present, extract the residue from evaporation with nitric acid with concentrated nitric acid or dissolved in aqua regia; excess oxidizing agent may be removed by evaporation, by potassium sulfite, or by stannous chloride before testing as above.

In all these procedures, microtechnic is to be employed, in refinement commensurate with the sensitivity required.

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Electroanalysis of Silver-Copper Alloys

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THE increased application of silver solders in fabricating copper alloy products creates a demand for rapid methods of determining copper and silver. Gravimetric methods are preferable for greatest accuracy. The American Society for Testing Materials provides an accurate method for silver solders in which silver is precipitated and filtered as the chloride, the filtrate is evaporated to fumes with sulfuric acid, nitric acid is added, and the solution is electrolyzed for copper (1). The evaporation of the filtrate, which must be done slowly and carefully to prevent loss by spattering, is the most tedious part of this method. This step is eliminated in the method presented, by the substitution of electrodeposition for the chloride precipitation of silver.

Experiments with electrolysis in hot nitric acid solutions gave fairly good separation of silver from copper, but the conditions were very strict and more than 0.2 gram of silver could not be weighed accurately because of poor adherence. Deposition of silver from ammoniacal solutions gave accurate results with a fair latitude in conditions. Complete separation from copper was obtained and the deposit was firmly adherent.

The electrolysis of silver in ammoniacal solution requires continuous stirring. Silver is deposited at the rate of about 0.0268 gram per minute, using 0.4 ampere, until deposition is practically complete. Hydrogen peroxide is then added to oxidize cuprous salts and to redissolve any particles of silver precipitated by inefficient stirring. Electrolysis is continued at 0.2 ampere until deposition is complete. Hydrogen peroxide is gradually destroyed during the latter stage of the electrolysis, leaving the electrolyte a nonsolvent for metallic silver and promoting complete deposition. Deposition of copper and less noble metals is prevented by the rapid circulation of cupric ions and oxygen from the anode. Cupric ions have a strong oxidation effect on metallic copper and less noble metals in ammoniacal solution, and by stirring sufficiently to prevent the formation of a protective layer of cuprous ions silver alone is deposited on the cathode. Stirring also helps to regenerate cupric ions at the anode. Nitrates present from the nitric acid used in dissolving the sample play an important part in preventing deposition of base metals and also help to reduce the resistance of the electrolyte, thereby keeping the solution cool and preventing loss of the ammonia.

Silver deposits completely from the ammoniacal solution and only unweighable traces have been found remaining in the electrolyte. Likewise only traces of copper are deposited with the silver, and if weighable amounts should be deposited because of inefficient stirring they are readily visible on the

surface of the silver. Silver has much less tendency to air-oxidize than copper, and its firm adherence on the cathode prevents loss when handled with the care usually taken in copper electrolysis. The deposition of silver from ammoniacal nitrate solution is comparable with that from alkaline cyanide solution. The complex salt prevents the formation of excess metallic ions around the cathode. This gradual breaking down of the complex ions promotes the formation of fine-grained deposits rather than coarse, loosely adherent crystals which are obtained from acid solutions.

The electrolyte from the silver determination is acidified with nitric acid and copper is determined electrolytically. The results compare favorably with other electrolytic copper determinations. The presence of considerable amounts of ammonium nitrate apparently helps in obtaining complete deposition of copper. Anodic loss proved to be less than 0.00005 gram when both silver and copper were electrolyzed using the same anode.

Procedure

Dissolve a 1-gram sample in a 300-cc. beaker, using 10 cc. of concentrated nitric acid and 20 cc. of water, and heat to expel lower oxides of nitrogen. Cool, and make the solution distinctly alkaline with ammonium hydroxide. Cool again to room temperature and add 10 cc. of concentrated ammonium hydroxide in excess. A cylindrical, platinum gauze cathode of about 100 sq. cm. and an anode of spiral-shaped platinum wire are required for electrolysis. The solution is diluted so that, when immersed, the top rim of the cathode is just above the solution level (about 150 to 200 cc.). Continuous stirring is required during the electrolysis and must be started before any current is used. (In the absence of a stirring device, efficient stirring may be obtained by passing a moderate stream of air bubbles from a glass tube with a capillary tip, adjusted to deliver at the bottom of the anode.)

Cover the beaker with split watch glasses and electrolyze at 0.4 ampere. Allow 10 minutes or longer over the time required for deposition of the silver at the rate of 0.027 gram per minute, then add cautiously from a pipet 10 cc. of a mixture of 1 part of U. S. P. hydrogen peroxide and 3 parts of distilled water. If the sample contains less than 10 per cent of copper, add only 4 cc. of the mixture. Do not direct the peroxide against the cathode. Reduce the current to 0.2 ampere and rinse the cover glasses. After 20 minutes, lower the beaker without interrupting the stirring and rinse the electrodes with a jet of distilled water, catching the rinsings in the beaker. Dip the cathode in alcohol and dry at 110° C. Any deposition of copper is evidence of inefficient stirring. This copper may be removed by continuing the electrolysis with an increased rate of stirring. If a yellowish color is evident on the cathode, dip the cathode in dilute hydrochloric acid after weighing, rinse, dry, and weigh again, taking the difference in weight as copper. With proper stirring, however, only metallic silver will deposit.

Acidify the electrolyte with concentrated nitric acid and add 10

cc. in excess. If any cloudiness develops due to cuprous oxide, add sufficient hydrogen peroxide to clear the solution. Cool the solution to room temperature, transfer to a 500-cc. beaker, and electrolyze for copper at 2.5 amperes.

Precautions

Interruption of the stirring during the early stages of the silver electrolysis will cause precipitation of considerable amounts of silver which remain undissolved on the bottom of the beaker. Insufficient stirring near the end of the electrolysis will cause deposition of copper. With these precautions in mind, the analyst may even double the rate of deposition and obtain accurate results by using a sufficient stirring rate.

TABLE I. PERCENTAGE OF SILVER IN REPRESENTATIVE SILVER SOLDERS

Sample No.	Electrolytic Method		Silver Chloride Method
1	15.10	15.12	15.13
2	15.19	15.20	15.21
3	20.26	20.23	20.26
4	20.08	20.06	20.06
5	45.10	45.12	45.12
6	45.04	45.03	45.07
7	64.99	65.00	65.01
8	64.98	65.00	65.00
9	50.22	50.20	50.20
10	50.21	50.22	50.23

Lead and metals that are more noble than copper will deposit with the silver. Lead deposits partly on the anode and partly on the cathode. Nickel present in amounts over 5 per cent in the sample causes poor adherence of silver and loss by dusting. Cathodes should be carefully stripped of all silver before heating to high temperatures or silver will alloy with the platinum.

Discussion

Table I shows results obtained by electrolysis as compared with the A. S. T. M. silver chloride precipitation method. The figures given in the silver chloride column were obtained by making several determinations until absolute checks were obtained. Five different types were selected as representative

of the more common silver solders. In addition to the silver, the compositions of the samples were as follows: 1 and 2 contained 80 per cent of copper and 5 per cent of phosphorus; 3 and 4 contained 45 per cent of copper and 35 per cent of zinc; 5 and 6 contained 30 per cent of copper and 25 per cent of zinc; 7 and 8 contained 20 per cent of copper and 15 per cent of zinc; 9 and 10 contained 15 per cent of copper, 17 per cent of zinc, and 18 per cent of cadmium.

TABLE II. WEIGHT OF SYNTHETIC SAMPLES

Sample No.	Silver Added Grams	Silver Deposited Grams	Copper Added Grams	Copper Deposited Grams
11	0.9998	0.9998	Nil
12	1.9996	1.9995	Nil
13	0.9998	0.9999	0.1
14	0.9998	0.9997	0.5
15	0.9998	0.9997	1.0
16	0.3862	0.3861	1.0
17	0.2536	0.2536	1.0
18	0.3506	0.3506	0.8169	0.8171
19	0.3057	0.3057	0.5075	0.5076
20	0.3029	0.3028	1.0122	1.0124

Table II shows the wide range of applicability of the electrolytic method. The silver and copper used in preparing the samples were carefully assayed by A. S. T. M. methods. Both metals were 99.98 per cent pure and the weights used in the tables are based on this metallic content. Both tables indicate that the error for silver may be due only to weighing. Slightly high results for copper may be due to air oxidation. The procedure apparently causes no abnormal error for copper.

Conclusion

Electrodeposition of silver from an ammoniacal nitrate solution is rapid and accurate. Copper may be determined rapidly by electrolysis from the acidified electrolyte. The method may be used for silver solders and various other silver alloys.

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Determining the Evaporation Rate of Solvents at High Temperatures

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THE recent technical literature has shown evidence of a considerable revival of interest in the subject of evaporation rate of solvents (1, 2, 5, 6, 7, 9). Most of the methods, however, have been designed to duplicate the conditions prevailing during the evaporation of solvents from varnish and lacquer films—i. e., the evaporation of thin layers of solvent into large volumes of air at approximately room temperatures. There is an extensive field for solvents in factory processing wherein the solvent is expelled with the aid of heat, and for which the foregoing methods of solvent evaluation do not appear to be adequate. The authors thought that it might be of interest at this time to report a method which has been used in this laboratory in substantially its present form for the past ten years for the purpose of evaluating petroleum solvents employed in the manufacture of rubber cements and compressed asbestos sheet doughs,

from which they are subsequently expelled with the aid of heat and air.

The features that distinguish this method from any of the methods above referred to are:

1. Approximately complete saturation of the air stream, thereby eliminating the time element and making results available directly as liters (or cubic feet) of air per cubic centimeter (or gallon) of liquid solvent.
2. Provision for maintaining sample at any desired temperature by vapor heating. Vapor heating is preferred to an air or water thermostat because of its high rate of heat input.
3. Provision for reading volume of sample at all stages of evaporation, without moving any part of the equipment.
4. Use of a large sample, permitting accurate determination of the dry point.

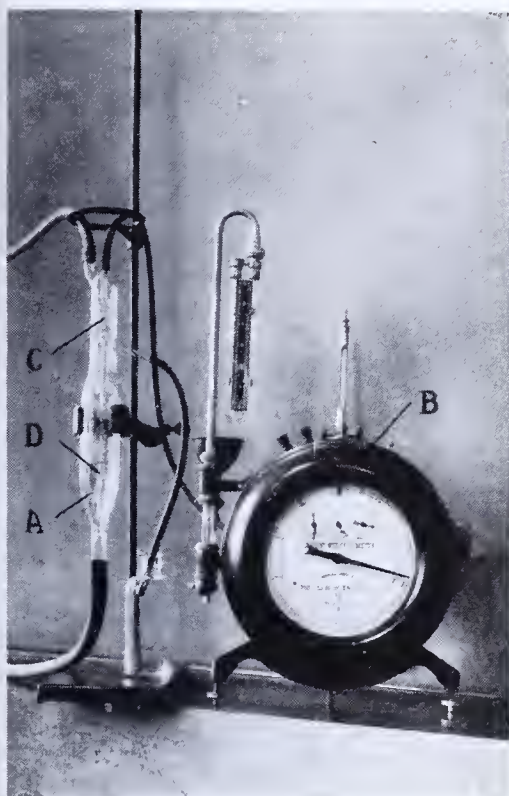


FIGURE I

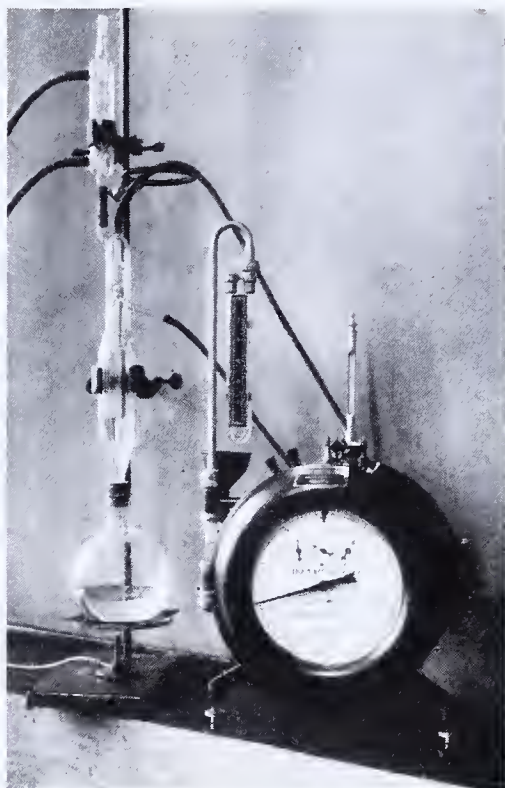


FIGURE II

In Figure II is shown the same apparatus arranged for heating by the vapor of any constant-boiling solvent, the ones the authors use being principally ethyl ether (b. p. 35°C.) and methanol (b. p. 65°C.).

In Figure III is shown a curve obtained on c. p. toluene at 100°C. , together with the curve calculated from the vapor pressure as given in International Critical Tables (3). The close adherence to theoretical saturation will be noted.

In Figure V will be noted the evaporation curves at 100°C. of two petroleum solvents, one light, A, as received from the refinery, and one heavy, B, as obtained from a recovery system. The corresponding distillation curves by the A. S. T. M. method are shown in Figure VI. Experience has shown that a product to be satisfactory for factory processing should be completely volatile in

The apparatus is shown in Figures I and IV arranged for heating by steam. The 100-cc. sample is inserted in the conical centrifuge tube, A, which is similar to the container used by Wetlaufer and Gregor (7) except that it has more graduations and is corrected for the volume of the inlet tube. The sample expands on heating to a new volume (about 110 cc.), which figure is noted and used as a divisor in the subsequent percentage calculations. If the sample boils partly below 100°C. , this method of correcting for volume cannot be employed; it is necessary in such cases to employ an arbitrary correction for volume based on extrapolation of the expansion rate of the solvent as determined at lower temperatures. After the sample has reached the temperature of the steam and any low-boiling fractions have boiled away the air stream is started through the wet test meter, B, preheater coil C, and 2-mm. inlet tube D. An air-drying tube was formerly employed but was found unnecessary and is omitted. The rate of air flow is not critical, provided the withdrawal of heat by evaporation is not rapid enough to lower the temperature of the sample appreciably. In practice the authors test gasolines at 300 cc. per minute, having found that there is practically no difference between curves obtained at this and at lower speeds. After 25 per cent has been evaporated they generally increase the rate to 500 cc. per minute. At intervals the air flow is shut off long enough to take simultaneous readings on the tube and meter. Results are plotted as liters of air, corrected to 21°C. , as a function of per cent evaporated based on an initial 100-cc. sample.

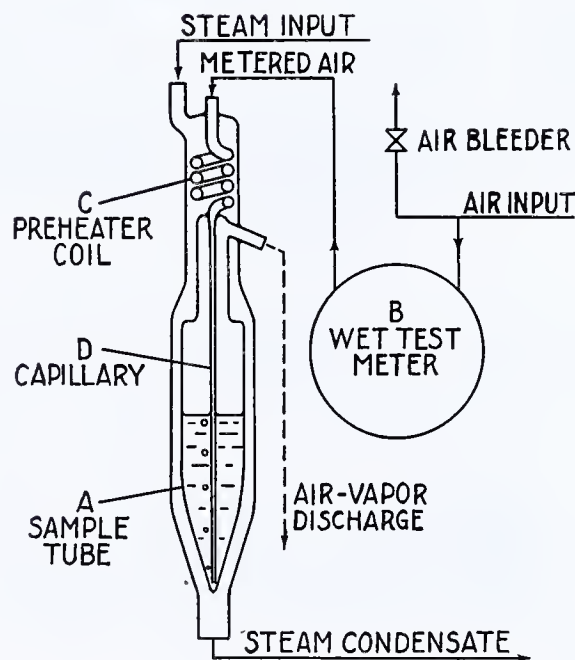
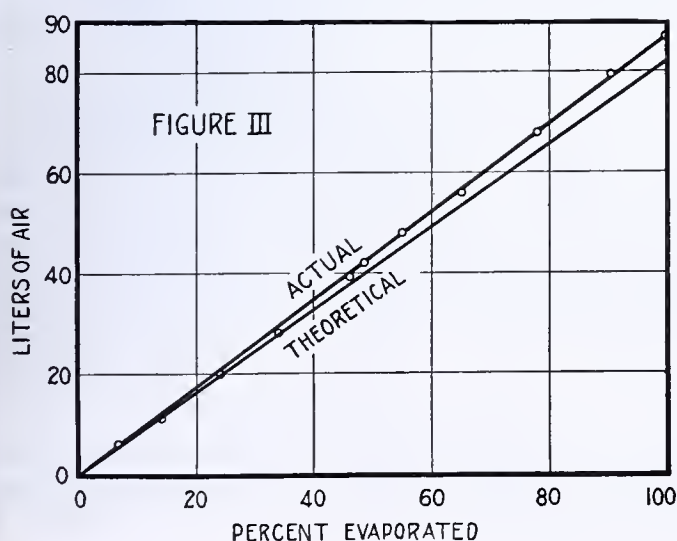
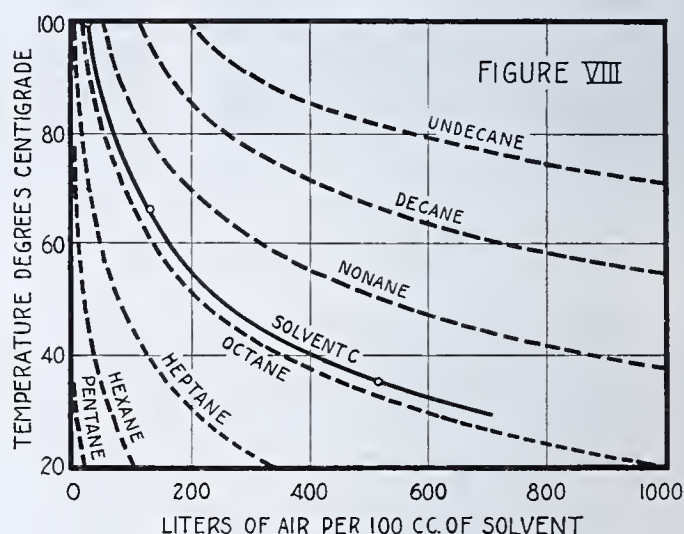
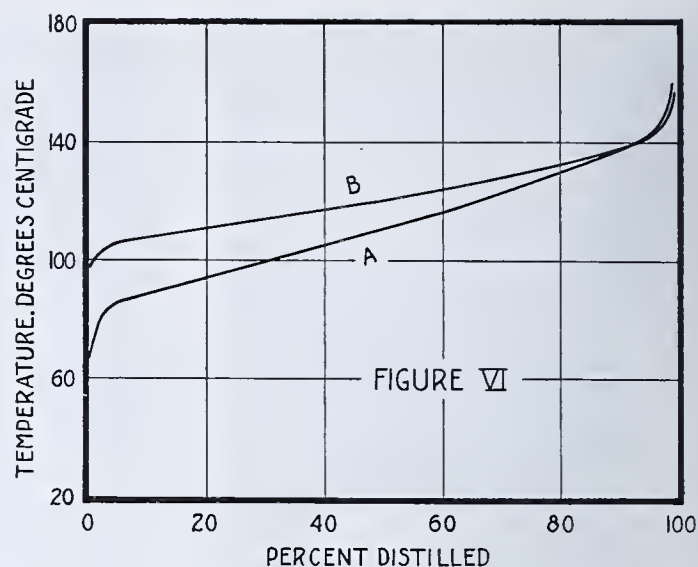
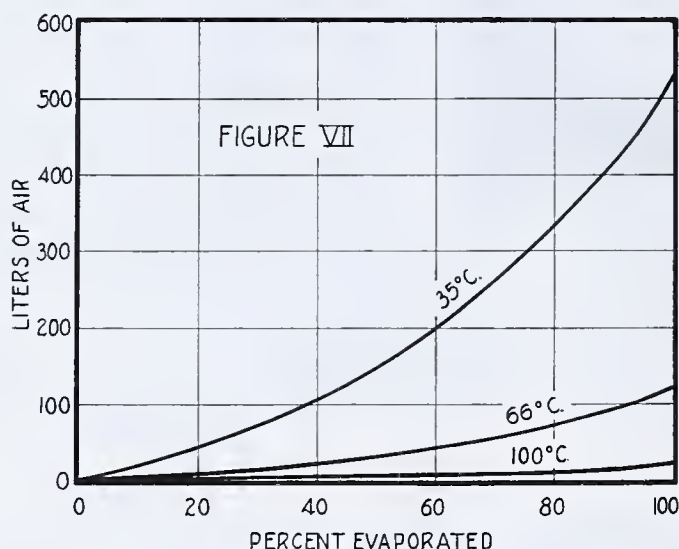
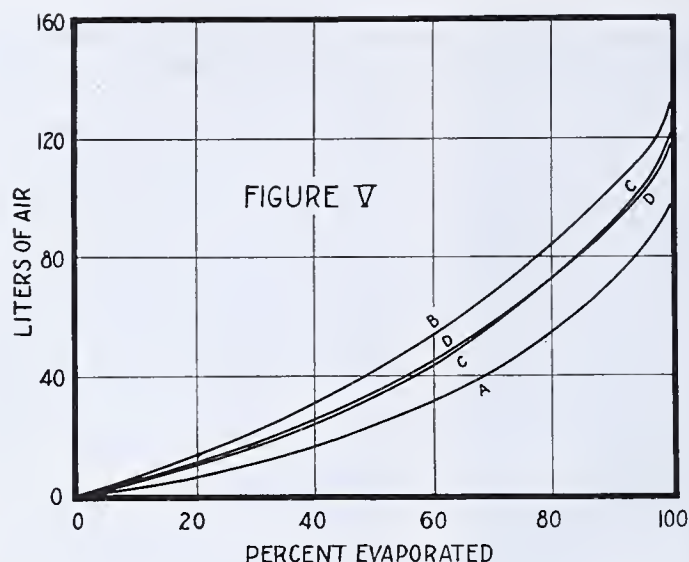


FIGURE IV. DIAGRAM OF APPARATUS



120 liters of air. As the passage of 120 liters through heavy solvent B leaves about 3 per cent residue, it might be expected that a somewhat similar residue would be found in factory processing, which was the case. On the other hand, solvent A used alone is unnecessarily volatile, resulting in heavy handling losses. Examination of evaporation curves for A and B suggests that a suitable solvent could be obtained by a blend of 6 parts of B and 4 parts of A, as indicated by the line D, the ordinates of which are interpolated between the ordinates of curves A and B on a uniform 60 to 40 ratio. Curve C is the evaporation curve actually obtained from such a blend, indicating that at least for the type of solvent employed the air volumes required for evaporation are approximately additive.

In Figure VII are shown the evaporation curves of solvent C at three temperatures. If the air volumes at 100 per cent evaporation of these curves are replotted (Figure VIII) as a function of temperature, and compared with similar curves for



pure straight-chain paraffin hydrocarbons, calculated from vapor-tension data given by Wilson (8), shown in dotted lines, the curve lies close to that of pure octane. It may be said, then, that in respect to the air volume required for complete evaporation, solvent C is equivalent to octane. It would be a fair assumption therefore that its "equivalent molecular weight," and consequently vapor volume, explosive limits, etc., at complete evaporation would correspond approximately to those of octane. This conception is very useful in designing fume systems, recovery equipment, etc., for handling the solvent, the necessary data being difficult to secure by other methods.

The formula used for computing the curves for the pure hydrocarbons is:

$$\text{cc. evaporated} = V \times \frac{T + 273}{294} \times \frac{A}{A - P} \times \frac{P}{760} \times \frac{273}{T + 273} \times \frac{M}{22.4} \times \frac{1}{D} = \frac{5.45 \times 10^{-5} \times V \times A \times P \times M}{(A - P) D}$$

where V = liters of ingoing air, measured at 21° C. and prevailing atmospheric pressure A
 T = temperature of evaporator tube (° C.)
 A = atmospheric pressure in mm. of mercury (assumed as 760 in computing curves above)
 P = vapor pressure of liquid at temperature T in mm. of mercury
 M = molecular weight
 22.4 = Avogadro's constant
 D = density of liquid at 21° C. (grams per cc., ρ)

The formula differs from that used by Hofmann (2) in the presence of the terms A in the numerator and $A - P$ in the denominator. It seems probable that evaporation test

methods, such as the one described above, which measure the volume of incoming air rather than volume of outgoing vapors, are not independent of barometric pressure, and the magnitude of the correction for barometric variation increases with the vapor pressure of the solvent—i. e., with the discrepancy between incoming and outgoing vapor volumes. A further correction should theoretically be applied to the authors' indicated meter readings, based upon the varying hydrostatic head created by the height of liquid in the sample tube. In practice such corrections for the type of solvent which the authors employ, and for the magnitude of barometric and hydrostatic pressure variations encountered, do not total more than 5 per cent, so that they can be ignored. A more rigid application of this method, especially to more volatile solvents, would necessitate taking these corrections into account.

It is also realized that the method is defective as a measure of the evaporation rates at incomplete saturation, such as occur in industrial applications, because, as pointed out by Lewis, Squires, and Sanders (4), it takes no account of the factor of variable diffusion rates of the various components. It would not be safe, therefore, to extend the method to mixtures of components of widely different molecular weights. For the particular type of solvents referred to, however, it has been found to furnish a good index to factory performance.

Acknowledgment

The writers wish to acknowledge the assistance of the Will Corporation, Rochester, N. Y., in developing the improved equipment and the permission granted by the officials of

the Garlock Packing Company to publish the above experimental data.

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RECEIVED April 30, 1936.

A New Colorimetric Procedure
Adapted to Selenium Determination

KURT W. FRANKE, ROBERT BURRIS, AND ROBERT S. HUTTON, South Dakota State College, Brookings, S. D.

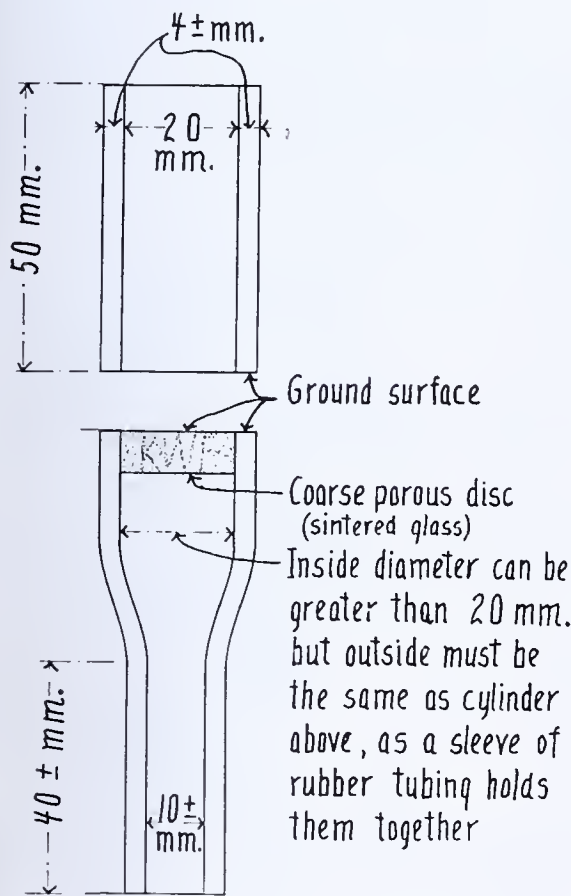


FIGURE 1. FILTER TUBE UNIT

THE instability of many colloidal sols necessitates the daily preparation of a new set of standards for colorimetric comparison. The following procedure provides for more permanent standards, eliminates turbidity difficulties, and also makes feasible the filing of the unknowns. A diagram of the apparatus is given in Figure 1.

A disk of filter paper (S. & S. 589 blue ribbon) is moistened and placed on top of the porous plate tube which has been attached to a suction filter flask. The cylinder is placed on the filter paper and held in place by a sleeve of rubber tubing. A mat of barium sulfate, freshly precipitated, is filtered onto this filter paper. For a disk 20 mm. in diameter a mixture of 20 cc. of 1 per cent barium chloride and 10 cc. of 1 per cent sulfuric acid provides a satisfactory mat for collecting colloidal selenium. This retains colloidal selenium as a thin surface layer against a standard white background. Little suction is applied when filtration of barium sulfate is first started, but a vacuum of about 30 cm. should be reached at the end of the mat formation and should be maintained during the filtration of the colloidal precipitate. The mat having been formed, the solution containing the colloidal precipitate is shaken and poured into the inclined filter

tube so as not to disturb the surface of the mat. The tube is now kept relatively full, in order that the pouring in of additional solution will not disturb the film already formed on top of the barium sulfate mat. When the filtration is completed the rubber sleeve is slid onto the lower tube while the upper one is held in place. The filter paper disk and mat are removed and allowed to dry for a few minutes. Two drops of glycerol are placed on a microscope slide, and the slide is inverted and pressed gently and uniformly in contact with the colloiddally covered mat surface. Colorimetric comparisons are made with standards prepared in the same way from standard solutions.

When the 20-mm. tube is used in the case of colloidal selenium, comparisons are best made in a range from 0.005 to 0.15 mg. of selenium, and the samples can be compared in this range with an accuracy of about 0.001 to 0.01 mg. Precision is of the same magnitude. Above this range gradations are not so sharp, unless a unit of larger diameter is used. It was determined that a mat one-half (14.1 mm. in diameter) the area of the 20-mm. mat would provide still greater sensitivity in lower amounts.

The red and blue forms of colloidal gold and Prussian blue were retained by a barium sulfate mat prepared as for selenium. Preliminary experiments indicate that for white or other light-colored sols black or other colored mats can be used.

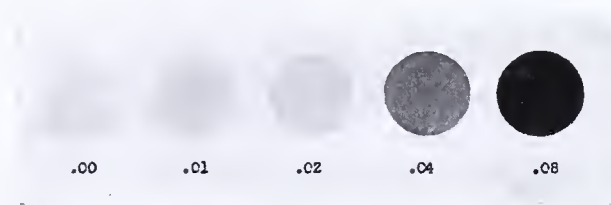


FIGURE 2. SELENIUM STANDARDS
One-half size, panchromatic process film, F 7.7, Wratten B filter, 2.5 minutes' exposure

It is obvious that this method can be used in micro ranges by substitution of mats of small diameter. For example, 0.001 mg. of iron converted to Prussian blue gives a very distinct color on a 14.1-mm. mat; a 5-mm. mat would give the same intensity with an eighth this amount of Prussian blue.

Conclusion

A method is described by which colored precipitates of colloidal fineness can be filtered onto a mat of barium sulfate. Permanent standards are produced and turbidity difficulties are removed. The procedure has been used for the estimation of 0.005 to 0.15 mg. of selenium with an accuracy of 0.001 to 0.01 mg.

RECEIVED July 18, 1936. With the permission of the Director of the South Dakota Agricultural Experiment Station as communication No. 23 from the Department of Experiment Station Chemistry.

Physical and Chemical Properties of Petroleum Fractions

II. Relations between Molecular Weight and Concentration in Dilute Solution

HARRY T. RALL AND HAROLD M. SMITH, Petroleum Experiment Station, Bartlesville, Okla.

The molecular weights of oils as usually calculated from either cryoscopic or ebullioscopic data generally change uniformly with concentration. This necessitates a series of determinations so that the curve through the determined values may be extrapolated to zero concentration.

There appears to be a relation between the slope of the molecular weight-concentration curve and the value of the extrapolated molecular weight. If this relationship is equated with the formula connecting the concentration and molecular weight, the result is an equation that will give the value of the extrapolated molecular weight from one determination.

Equations of this character are given for benzene and ethylene bromide. Comparisons of calculated and actual results are also given which show that for the data presented the suggested method applies fairly well.

IT HAS long been observed, in the determination of molecular weights of petroleum fractions by the cryoscopic method in benzene, that the apparent molecular weight of the solute as calculated by the ordinary formula

$$m = K \frac{M_s}{\Delta} \times \frac{w}{W} \quad (1)$$

increases with the concentration of the solute. Equally true, but perhaps less commonly known, is the case of solvents in which the deviation is negative, as for cyclohexane in the cryoscopic method and carbon tetrachloride or cyclohexane in the ebullioscopic method. So far as the authors can ascertain, no adequate explanation of these departures from theoretical solution laws has been made. However, the reason for these deviations is not the subject of this paper; rather it is recognized as a fact, and an attempt is made to utilize it to simplify the determination of the molecular weight of petroleum fractions.

Empirical Relationships

FitzSimons and Thiele (1) report an attempt to devise a formula from which the extrapolated molecular weight could be calculated from a single observation of molecular weight by the freezing point depression method. Their formula, stated to be applicable to benzene and cyclohexane, is given as

$$M = (K - 2\Delta) \frac{w}{W} \cdot \frac{M_s}{\Delta} \quad (2)$$

which may be rearranged as

$$M = m \left(\frac{K - 2\Delta}{K} \right) \quad (3)$$

where M is the extrapolated value of molecular weight, m the observed molecular weight as calculated by Formula 1, w/W the concentration in grams of solute per gram of solvent, M_s the molecular weight of the solvent, K the molar cryoscopic constant, and Δ the depression in degrees Centigrade. It appears that Equation 3 implies a definite percentage decrease over Formula 1 for each oil per degree depression, the percentage varying with the solvent, being smaller the larger

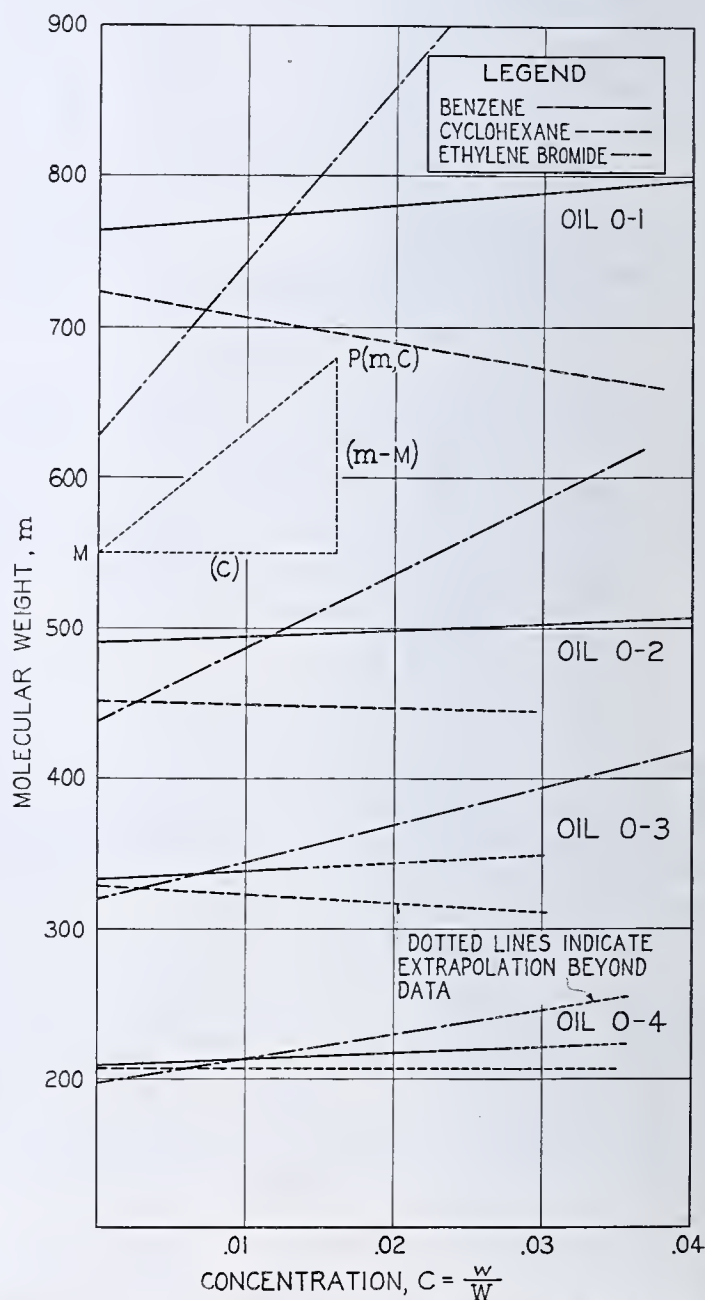


FIGURE 1. RELATIONSHIP BETWEEN OBSERVED MOLECULAR WEIGHT AND CONCENTRATION FOR THREE CRYOSCOPIC SOLVENTS

the cryoscopic constant. The experience of this laboratory is that such a simple correction will not apply generally to all oils or to all solvents. It definitely cannot be applied to solvents in which the slope of the molecular weight-concentration curve is negative.

During the past few years this laboratory has had occasion to make numerous molecular weight determinations by both the cryoscopic and ebullioscopic (Menzies-Wright) methods with pure and impure solvents and with and without dehydrating agents (2). It has been observed that the slope of the molecular weight-concentration curve depends for the most part upon the molecular weight of the solute. This observation is probably not precisely true, but it is believed to be sufficiently exact for the intended use of the relationship. Further work, if it does not completely invalidate the equations developed on this assumption, will only correct them. The equations are entirely empirical and are subject to correction or abandonment as more and more data are accumulated.

Figure 1 shows curves obtained by plotting observed cryoscopic molecular weights as calculated by Equation 1 against concentration of solute for four different oils in three different solvents (2). The discrepancy between the extrapolated values of molecular weight of the four oils in the various solvents may be due to impurities and moisture and will be disregarded; the slope of the curves is the point to which attention will be directed. It will be observed that the slope for benzene and ethylene bromide increases and for cyclohexane decreases as the molecular weight of the oils increases.

Table I gives the equations of all the curves of Figure 1 and also those for six ebullioscopic solvents. The method of averages was applied to the cryoscopic and ebullioscopic data in the derivation of these equations. From inspection of the equations in Table I the thought occurs that there might possibly be some relation between the extrapolated value of molecular weight, M , and the slope, S , of the curve. Figure 2 shows the result of plotting S against M . While there are several irregularities in the data from which this family of curves was derived, there seems to be a definite tendency for the slope to increase or decrease as molecular weight increases, and all curves appear to originate at the origin. Thus when benzene is used as a solvent in cryoscopic determinations the linear equation, calculated by the method of least squares

$$S = 1.15 M \tag{4}$$

passes through the origin and satisfies all the points for this solvent fairly well. In a like manner the relation, not necessarily linear, between slope S and molecular weight M could be determined for each solvent, provided the molecular weights of sufficient oils were determined to make the equation certain. Once this relation is known it becomes simply a problem in algebra to apply it in developing an equation from which M can be determined from a single observation of m on any other sample of unknown molecular weight. Referring to Figure 1, assume that the apparent molecular weight of such an oil has been determined and the point P located. It is apparent that the extrapolated molecular weight can be represented by the equation

$$M = m - SC \tag{5}$$

which is a transposed form of those equations reported in Table I. This equation can be rewritten to evaluate S and this value substituted in Equation 4 (or similar equations for

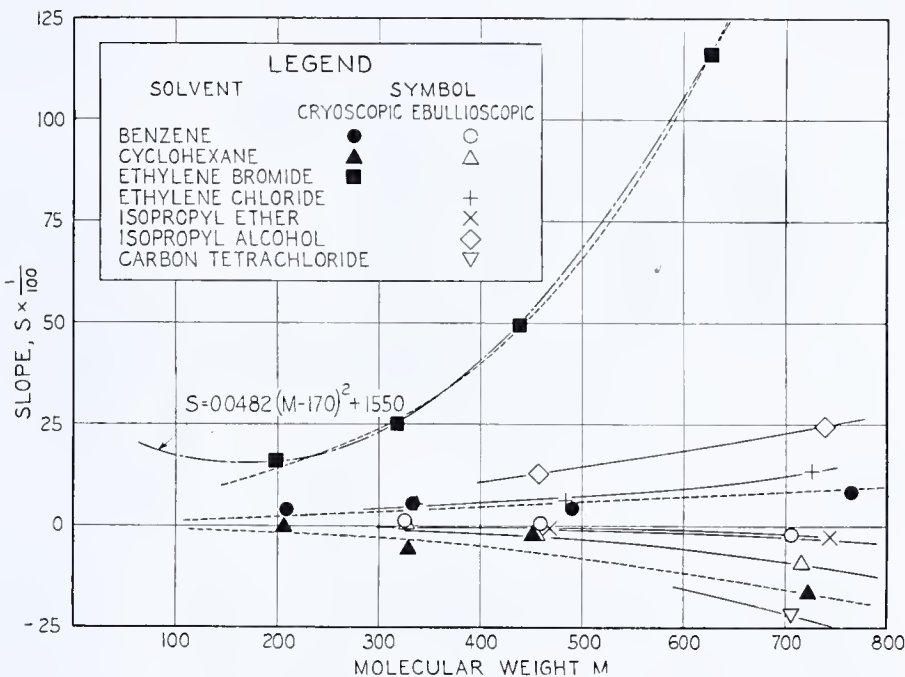


FIGURE 2. SLOPE-MOLECULAR WEIGHT RELATIONSHIP FOR SEVEN SOLVENTS

various solvents) from which M can be determined in terms of known quantities. Thus the equation

$$M = \frac{K \frac{w}{W} \frac{M_s}{\Delta}}{1 + 1.15 \frac{w}{W}} = \frac{m}{1 + 1.15 C} \tag{6}$$

is obtained for benzene (cryoscopic). It might be mentioned that the equation

$$M = \frac{1.125 C \left[\frac{M_s}{\Delta} K - 200 \right]}{1.125 + C} = \frac{m - 200 C}{1 + 0.889 C} \tag{7}$$

accommodates the authors' own data somewhat more closely than Equation 6. This equation does not include the origin and therefore assumes some slope for zero molecular weight which it is believed is not in accord with the general trend of the data for the several solvents studied (Figure 2).

TABLE I. SLOPE-MOLECULAR WEIGHT RELATIONSHIPS FOR SEVEN SOLVENTS

Solvent	Method	Equation ^a	
		<i>M</i>	<i>S</i>
Oil O-1			
Benzene (A-1)	Cryo.	<i>m</i> = 763.7 +	855.2 <i>C</i>
Benzene (A-3)	Ebull.	<i>m</i> = 705.6 −	215.0 <i>C</i>
Cyclohexane (B-1)	Cryo.	<i>m</i> = 722.6 −	1674.0 <i>C</i>
Cyclohexane (B-3)	Ebull.	<i>m</i> = 716.1 −	948.0 <i>C</i>
Ethylene chloride	Ebull.	<i>m</i> = 725.1 +	1363.0 <i>C</i>
Isopropyl ether	Ebull.	<i>m</i> = 743.0 −	310.0 <i>C</i>
Isopropyl alcohol	Ebull.	<i>m</i> = 738.1 +	2446.0 <i>C</i>
Ethylene bromide	Cryo.	<i>m</i> = 626.5 +	1160.0 <i>C</i>
Carbon tetrachloride	Ebull.	<i>m</i> = 704.9 −	2166.0 <i>C</i>
Oil O-2			
Benzene (A-1)	Cryo.	<i>m</i> = 490.6 +	430.5 <i>C</i>
Benzene (A-3)	Ebull.	<i>m</i> = 459.8 +	35.0 <i>C</i>
Cyclohexane (B-1, B-2)	Cryo.	<i>m</i> = 451.5 −	208.0 <i>C</i>
Cyclohexane (B-3)	Ebull.	<i>m</i> = 455.6 −	229.0 <i>C</i>
Isopropyl ether	Ebull.	<i>m</i> = 468.9 −	31.3 <i>C</i>
Isopropyl alcohol	Ebull.	<i>m</i> = 457.7 +	1270.0 <i>C</i>
Ethylene bromide	Cryo.	<i>m</i> = 438.0 +	4920.0 <i>C</i>
Ethylene chloride	Ebull.	<i>m</i> = 484.6 +	626.0 <i>C</i>
Oil O-3			
Benzene (A-2)	Cryo.	<i>m</i> = 333.4 +	535.4 <i>C</i>
Benzene (A-3)	Ebull.	<i>m</i> = 325.9 +	121.7 <i>C</i>
Cyclohexane (B-2)	Cryo.	<i>m</i> = 328.9 −	595.5 <i>C</i>
Cyclohexane (B-3)	Ebull.	<i>m</i> = 326.9 +	47.1 <i>C</i>
Ethylene chloride	Ebull.	<i>m</i> = 336.8 +	542.2 <i>C</i>
Ethylene bromide	Cryo.	<i>m</i> = 318.7 +	2500.0 <i>C</i>

^a C = concentration = $\frac{w}{W}$.

TABLE II. APPLICATION OF EQUATION 6 TO MOLECULAR WEIGHT DATA

Oil 0-1			Oil 0-2			Oil 0-3			Oil 0-4		
$\left(\frac{C}{W}\right)$	$\left(\frac{m}{K \frac{w}{W} \Delta}\right)$	M from Eq. 6	$\left(\frac{C}{W}\right)$	$\left(\frac{m}{K \frac{w}{W} \Delta}\right)$	M from Eq. 6	$\left(\frac{C}{W}\right)$	$\left(\frac{m}{K \frac{w}{W} \Delta}\right)$	M from Eq. 6	$\left(\frac{C}{W}\right)$	$\left(\frac{m}{K \frac{w}{W} \Delta}\right)$	M from Eq. 6
0.02118	778.8	760.3	0.02734	498.6	483.6	0.01032	342.3	338.3	0.00719	212.8	211.1
0.04082	799.6	763.7	0.05677	514.1	482.6	0.02033	348.0	340.1	0.01391	215.5	212.1
0.06159	820.2	766.0	0.07871	525.3	481.7	0.03295	355.8	342.8	0.02140	217.3	212.1
0.08332	828.8	766.3	0.10825	538.2	478.6	0.02400	351.1	341.6	0.00546	214.9	213.6
0.01626	778.5	764.2	0.01166	501.2	494.6	0.03598	358.3	344.1	0.01054	213.2	210.6
0.03472	794.4	763.9	0.02462	501.6	487.8	0.00603	336.3	334.0	0.01602	215.8	211.9
0.05587	814.6	765.4	0.03942	506.2	484.2	0.01456	340.7	335.1	0.02468	218.8	212.8
0.07817	829.6	761.2	0.06195	519.3	484.8	0.02542	345.1	335.3	0.00485	206.4	205.3
.....	0.01016	494.5	488.8	0.03711	352.2	337.8	0.01091	214.0	211.3
.....	0.00503	495.8	492.9	0.04722	356.4	338.0
.....	0.02021	495.3	484.0	0.00727	333.9	331.1
.....	0.03544	505.0	485.2	0.01561	339.3	333.3
.....	0.05220	511.0	482.1	0.02615	342.5	332.5
.....	0.07307	522.7	482.2	0.03517	346.9	333.4
Extrapolated values for M	763.7	763.7	490.6	490.6	333.4	333.4	209.3	209.3
Average	805.6	762.6	509.2	485.2	346.3	337.0	214.3	211.2

Table II gives the results of cryoscopic molecular weight determinations in benzene made on four oils calculated according to the usual equation and according to Equation 6. In Figure 3, where these same data are plotted, the effect of applying Equation 6 is apparent, and the curves indicate that the result probably is fairly adequate for the purpose. However, it is believed that additional data, carefully obtained, might lead to an even better formula universally applicable to the determination of the molecular weight of petroleum and its fractions with benzene in the cryoscopic method.

It is realized that several laboratories have reported molecular weight *vs.* concentration curves not in harmony with some of those presented in this paper. Data from other petroleum laboratories working with apparatus similar to the authors' have been examined and considerable agreement has been found.

Application of Equations to Data

The applicability of Equation 6 to some such data is shown in Figure 4 where the results obtained by eight laboratories as well as the authors' are graphed for the four oils (2) reported in Table I. At intervals are shown curves that represent the ideal slope all data would have to assume to accommodate Equation 6 perfectly. Any data falling on these ideal curves or roughly parallel to them would give the extrapolated

molecular weight, M , of any sample from cryoscopic data in benzene if calculated according to Equation 6. The agreement is not perfect but it is encouraging.

It is assumed in the case of benzene (cryoscopic) that the relation between S and M is linear. This assumption is probably near enough to fact for the purpose of formulating Equation 6, but additional data would probably show it to be a curve. Most of the other data of Figure 2 cannot be represented suitably by straight lines. Thus the equation of the parabola

$$S = 0.0482 (M - 170)^2 + 1550 \quad (8)$$

is in agreement with the authors' data for ethylene bromide. The curve, however, does not pass through the origin and therefore cannot apply to data below $M = 250$, as can be readily understood by inspection of Figure 2. An equation for ethylene bromide corresponding to Equation 6 for benzene can be developed from Equation 8.

$$M = \frac{(16.39 C - 1) + \sqrt{1 - (32.78 - 0.1928 m) C - 298.9 C^2}}{0.0964 C} \quad (9)$$

This formula corrects all the data obtained in ethylene bromide so nearly perfectly that any single determination might have been accepted with confidence that in no case would the error from the extrapolated value be very great, considering that the rise in apparent molecular weight (as calculated by the ordinary formula) with concentration is unusually great. Of course, the result cannot be any more accurate than is the single determination itself. If it is in error (datum does not lie on the molecular weight-concentration curve) then the results of applying the above formula will also be in error by a corresponding amount plus any additional error that might be incorporated in the formula itself. The latter is small in this particular case. Table III gives the result of applying the formula to the data from one of the oils.

Equation 9 is entirely too cumbersome for convenience, but it indicates what can be done even in the case of such a solvent as ethylene bromide, where the increase of apparent molecular weight with concentration is exceptional. Figure 5 shows clearly how Equation 9 reduces the data obtained for oil O-1 in ethylene bromide to nearly a horizontal line. Since Equation 8 fits the data points for oils O-2, O-3, and O-4 as accurately as it does the data point of O-1 (Figure 2), it is obvious that molecular weight data for these oils will plot just as nearly horizontal if calculated by Equation 9 as do the data for oil O-1. Tables II and III indicate the error possible in accepting an "average" molecular weight when calculated by the usual formula, particularly where large

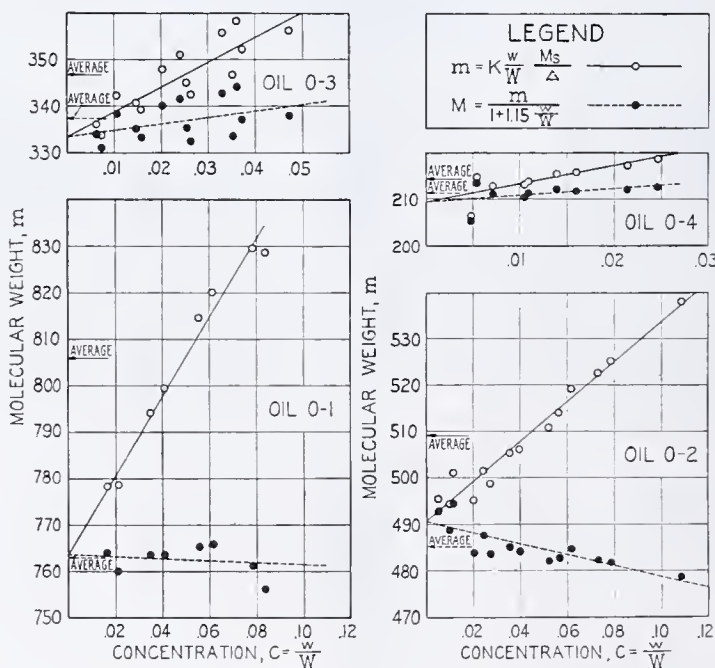


FIGURE 3. APPLICATION OF EQUATION 6 TO MOLECULAR WEIGHT DATA IN BENZENE

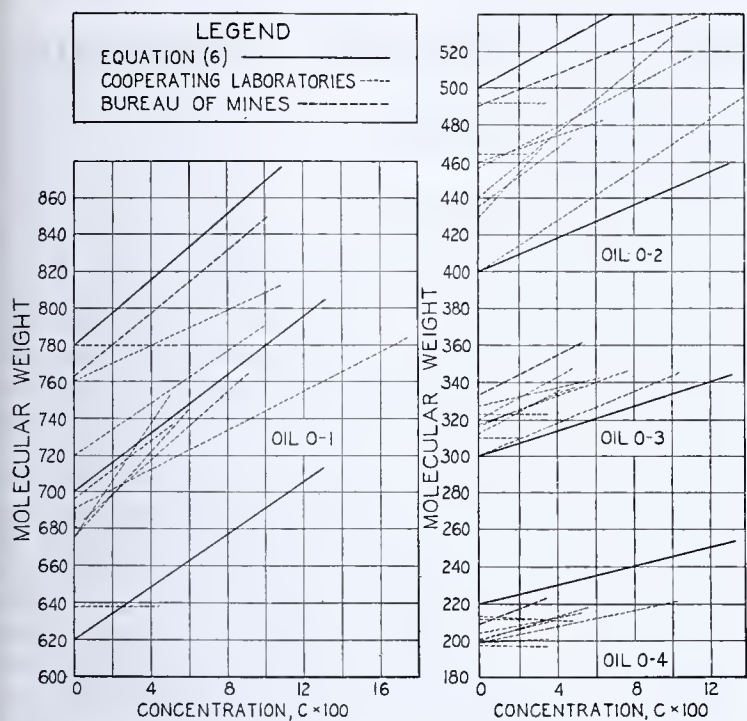


FIGURE 4. GRAPHICAL COMPARISON OF DATA FROM NINE LABORATORIES WITH EQUATION 6

concentrations of solute are employed or solvents giving a steep molecular weight-concentration curve are used.

Discussion

It should be understood, of course, that these equations are entirely empirical and are based upon the molecular weights of the four petroleum oils studied. They are therefore subject to revision or rejection as further data are accumulated. However, the attention of all petroleum laboratories is directed to these equations and their development in the hope that confirmation or conflict may be discovered in data of these laboratories. These equations are recommended for use primarily where only one determination of apparent molecular weight is made. The procedure of determining apparent molecular weight at various concentrations and extrapolating to zero concentration is still to be considered the safest practice. However, if only one determination is made, equations such as 6 and 9 appear to the authors to be a logical approximation, particularly if in that determination a high concentration of oil is used or a solvent whose slope-molecular weight curve deviates rapidly from the molecular weight axis.

TABLE III. APPLICATION OF EQUATION 9 TO MOLECULAR WEIGHT DATA

(Oil O-1 in ethylene bromide)		
C $\left(\frac{w}{W}\right)$	$m =$ $\left(K \frac{w}{W} \frac{M_s}{\Delta}\right)$	M from Equation 9
0.01818	808.1	609.8
0.02030	838.0	614.0
0.03873	1078.5	627.4
0.02717	946.1	628.5
0.01744	850.8	638.7
0.00290	632.5	601.8
0.05427	1267.7	630.0
0.03611	1048.2	628.4
0.02260	897.5	630.9
0.00855	737.5	635.8
0.00348	671.2	628.9
0.00612	643.8	583.6
0.00646	697.8	622.9
0.00249	653.4	625.0
0.00914	771.5	653.5
0.01251	803.1	645.9
Extrapolated value for M		626.5
Average		625.3

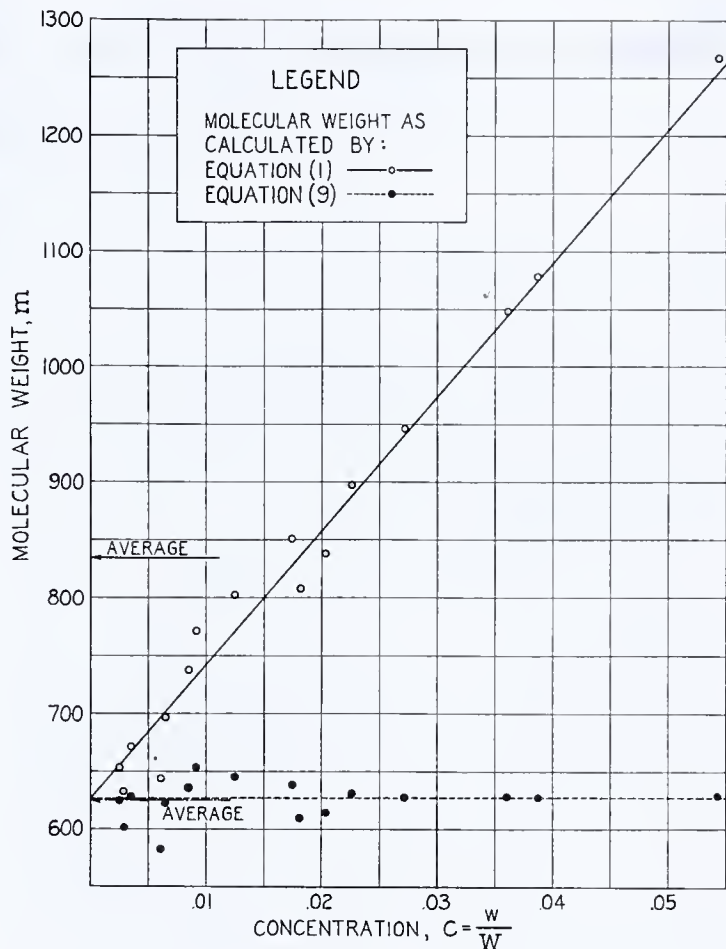


FIGURE 5. APPLICATION OF EQUATION 9 TO MOLECULAR WEIGHT DATA IN ETHYLENE BROMIDE

Considering the curves shown in Figure 2, it would seem that some idea could be obtained of the relative desirability of the solvents when used in cryoscopic or ebullioscopic determinations. Thus, ethylene bromide swinging sharply away from the molecular weight axis indicates a rapid departure from ideal solution laws as the molecular weight increases. Conversely, those curves lying near the molecular weight axis would indicate less deviation from solution laws. From this standpoint benzene used either cryoscopically or ebullioscopically should be the preferred solvent. However, other factors might also influence the choice of solvent, such as the solubility of water and of the sample to be determined, the value of K , the convenience of the freezing or boiling point, and probably numerous other conditions, some of which might be peculiar to special laboratories or equipment. Thus, in the authors' apparatus (2) cyclohexane is a satisfactory cryoscopic solvent. The authors do not believe it would be as satisfactory as benzene in the usual type of apparatus because its low heat of fusion necessitates good agitation and rapid determination of freezing point before the concentrating of the solvent due to crystallization becomes appreciable. Similarly, from inspection of Figure 2, isopropyl ether would seem to be as satisfactory an ebullioscopic solvent as benzene. However, the property of frothing and the limited solubility of petroleum oils in this solvent are serious objections to its use in the Menzies-Wright apparatus.

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Measurement of Flow Rates of Hot-Oil Streams by the Dilution Method

Study of Naphthenic Acid for Use as Diluent

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For test purposes the dilution method of measurement is desirable for determining rates of flow of internal recirculating hot-oil streams on commercial cracking units and distillation equipment. Previously this method has not been used for oil streams because there was available no material which was known to be satisfactory as a diluent.

Commercial naphthenic acid produced as a by-product of the refining of naphthene-base crudes has been found suitable for use in this service. Its concentration may be determined accurately even in dilute solutions with the modified method herein reported, it is sufficiently stable, it is non-corrosive, and its cost is moderate.

Tests on a commercial cracking unit indicated that charge rates determined by the dilution method, using naphthenic acids as the diluent, checked within 2 per cent the rates determined by tank gagings.

THE accurate measurement of flow rates of internal recirculating streams in commercial cracking units and distillation equipment is of considerable importance in petroleum refineries, particularly in connection with experimental work. Unfortunately the usual types of commercial meters are not suitable for accurate measurements in this service, partly because the flow is generally pulsating and partly because of inadequate knowledge of the temperature-pressure-volume relationships of oils at the conditions encountered. Although accurate results could be obtained by cooling the recirculating streams, discharging to tankage where accurate gagings would be possible, and reheating and returning to the system, this would obviously be a very costly procedure and could be applied only in very special cases.

Frequently, during experimental work, flow rates are maintained sufficiently constant so that a determination of rate over a relatively short time will be representative of the rates over a longer period. In other cases meters of some type may be available which will give accurate measurements if calibrated under the conditions at which they operate. Under these circumstances—that is, for calibrating purposes or for other conditions where the determination of rate over a relatively short time is useful—the dilution method of measurement has many advantages.

The Dilution Method

The dilution method of measurement is essentially simple. It consists merely in the introduction of some foreign material, at a constant and known rate, into the stream which is to be measured, and determination of the concentration

of the foreign material in the flowing stream. Knowing the rate of flow of the diluent stream and the concentration of the diluent in the main stream, the rate of flow of the main stream may easily be calculated.

This method may be used with negligible changes in existing piping, requires little equipment, and, if proper precautions are taken, is accurate. It has been used from time to time for the measurement of steam, air, gas, and water, but there is no record of its having been used successfully for hot oils, probably because there was available no material which was known to be satisfactory for use as a diluent. It was the object of the investigation here reported to find such a material.

SELECTION OF DILUENT. The major requirements of a satisfactory diluent for use in measuring hot-oil streams are as follows:

1. It must be inexpensive.
2. Its quantitative determination must be rapid and accurate.
3. It must be thermally stable at the temperature and pressure conditions in recirculating hot-oil streams of commercial cracking units.
4. It must not react with the material being measured.
5. It must be a liquid at hot-oil recirculating line conditions.
6. It must be readily soluble in the material which it is desired to measure.
7. It must be noncorrosive.
8. It must not harm the product from the unit.

Obviously the number of materials which will satisfactorily meet these requirements is rather limited. Preliminary consideration was given to a number of classes of materials, including (1) naphthenic acids and their soaps, (2) stearic acid and its soaps, (3) natural fats and oils, (4) antimony trichloride, (5) oil-soluble hydrocarbon derivatives of heavier metals, and (6) colloidal solutions.

A brief consideration was sufficient to eliminate some of these groups of compounds immediately. Group 6 was discarded because of the possible difficulty of obtaining sufficient mixing to ensure a homogeneous solution. Group 5 was eliminated because of the probable cost of such compounds. Of the remaining four groups, group 1 appeared the most promising.

Suitability of Naphthenic Acids

Naphthenic acids are produced in many refineries as a by-product from the running of naphthene-base crudes for lubricating oils. Generally the over-all lubricating distillate fraction from these crudes is rerun under vacuum over caustic. The bottoms from the vacuum distillation, which contain approximately 40 per cent of sodium naphthenates, are treated with 66° Bé. sulfuric acid and the resulting naphthenic acid-oil mixture is redistilled to produce various grades of commercial naphthenic acids. Typical tests of two different grades are shown in Table I.

It was immediately apparent that naphthenic acids meet a number of the requirements for a satisfactory diluent. Obtained as a by-product of lubricating oil manufacture they are relatively inexpensive. The literature indicates that they are fairly stable thermally although at high temperatures

they decompose into hydrocarbons, acetic acid, and phenols. They satisfy the requirement of solubility and it did not seem likely that they would react to an appreciable extent with the oils to be measured. Their introduction would not be harmful to the products from a cracking unit, since they would either be eliminated in the fuel or would be decomposed to form principally hydrocarbons. Even assuming that naphthenic acids or their decomposition products would be undesirable in special cases, they would be present in such small concentrations for such a short time that they would have a negligible effect on the final product.

TABLE I. TYPICAL TESTS

Acid value, mg. of KOH per gram of sample	139	93
Saponification value, mg. of KOH per gram of sample	144	94
Nonsaponifiable, %	22	42
Viscosity, Saybolt Universal at 98.89° C. (210° F.)	96	121
Gravity, ° A. P. I.	13.7	14.4
Flash	197.78° C. (388° F.)	207.22° C. (405° F.)
Fire	226.67° C. (440° F.)	240.56° C. (465° F.)
Pour	-6.67° C. (20° F.)	4.44° C. (40° F.)

Because of the range of molecular weights of these acids, a fraction may be selected which will be liquid at hot-oil recirculating line conditions. A comparison of A. S. T. M. distillations of a sample of commercial naphthenic acid with those of representative recirculating oil streams is shown in Table II.

TABLE II. A. S. T. M. DISTILLATIONS OF NAPHTHENIC ACID AND REPRESENTATIVE RECIRCULATING STOCKS

	Naphthenic Acid	A	B	C	D	E
I. B. P., ° F.	620	351	446	424	234	258
10%	666	440	559	472	430	450
20%	674	460	608
30%	682	472	648
40%	686	489	681
50%	692	502	704	539	490	561
60%	702	620

Since the naphthenic acids have as high a boiling range as the recirculating stocks, it is apparent that there will be no vaporization of this material when introduced into a liquid stream of the oil.

Previous work had shown that naphthenic acids and their decomposition products were no more corrosive than normal cracking stocks. The corrosion rates of steel specimens suspended in the vapor space of the reaction chamber on a laboratory cracking unit were found to be 0.46 cm. (0.184 inch) per year with gas oil charge and 0.358 cm. (0.143 inch) per year when charging naphthenic acids, both based on 100 per cent operating time.

Since it was not definitely known that the concentration of naphthenic acids in dilute oil solutions could be determined with sufficient accuracy or that the acids were entirely stable and nonreactive in the presence of hot oils, it was necessary to investigate these items experimentally.

Investigation of Analytical Method

It was believed that the concentration of naphthenic acids in oil could most easily be established by analysis for acidity. To determine whether the analysis could be made with sufficient accuracy with a low concentration of acid, a blend of 2.5 per cent naphthenic acid in recirculating stock D was prepared and the acid value determined by the ordinary method, consisting of adding neutralized alcohol, heating the resulting mixture, and titrating with 0.1 N potassium hydroxide, using phenolphthalein indicator. It was found that this method was not accurate, since the color of the oil interfered with the determination of the end point. Other indicators having color changes at about the same pH value as phenolphthalein were also tried but with no better success. Since these results were not encouraging, it was concluded that the determination could be made accurately only by separating the acid

from the oil. Accordingly, several variations of the usual procedure were tried with varying degrees of success. The following analytical procedure is the method finally adopted for nonviscous dark-colored distillate oils of the type found in hot-oil recirculating streams:

A 10- to 50-gram sample is weighed into an Erlenmeyer flask. The size of sample used depends on the percentage of naphthenic acid present and its acid value. For 2.5 per cent of 125 acid value naphthenic acids a 15-gram sample is satisfactory. Proportionately larger samples are desirable for lower acid concentrations. To the sample are added 100 cc. of neutral alcohol and a few drops of phenolphthalein indicator. The solution is heated to the boiling point and the boiling continued for several seconds, following which it is titrated with 0.1 N potassium hydroxide. When near the end point a small amount of water is added by means of a wash bottle to aid in separating the oil layer from the alcohol. The titration is continued with vigorous shaking and just enough water is added after each addition of potassium hydroxide to separate the two layers. A faint pink color in the alcohol-water layer designates the end point.

When analyzing prepared samples containing 1 per cent or more of naphthenic acid using the above method, the individual determinations generally checked the calculated acid values within 1 per cent. Occasionally, however, the determined acid values differed as much as 2 or 3 per cent from the calculated values and it is therefore considered desirable to make at least four or five determinations and average the results. Since the analyses can be made rapidly, this is not considered a serious handicap.

A comparison of determined with calculated acid values for several prepared samples of naphthenic acids in recirculating stocks is shown in Table III. In each case the determined value is the average of five analyses.

TABLE III. ACID VALUES

Sample	Naphthenic Acids %	Acid Value by Analysis	Acid Value Calculated	Error %
1	2.7	3.39	3.38	+0.3
2	2.5	3.14	3.17	-0.9
3	0.9	1.19	1.19	0.0
4	0.7	0.934	0.916	+2.0

The accuracy of 1 per cent or better which can be attained with naphthenic acid concentrations of over 1 per cent is considered entirely adequate and the addition of 1 to 2 per cent of naphthenic acids to the stream to be measured is not considered excessive.

It is emphasized that the analytical method described above is applicable only to low-viscosity distillate stocks. This is the type of material generally present in recirculating streams of cracking units where the dilution method of measurement will be of greatest value. For viscous residual stocks electro-metric titration gave good results. Although the latter method was not tried on distillates, it would undoubtedly be satisfactory in this case also but has the disadvantage of requiring equipment which is not available in all laboratories.

Thermal Stability of Naphthenic Acids

A satisfactory analytical procedure having been developed, the next step was to determine the stability of naphthenic acids at temperature and pressure conditions maintained in hot-oil recirculating lines of commercial units. It is not necessary, of course, that the diluent be absolutely stable at high temperature. The only requirement is that it shall not undergo an appreciable change between the point of introduction of the diluent into the stream to be measured and the point of withdrawal and cooling of the sample of diluted oil. The distance between points of introduction and sampling may be made as short as desired, subject only to the limitation that sufficient distance must be allowed to ensure thorough mixing of the diluent with the flowing stream.

As a basis for determining the time during which the diluent would be subjected to high temperatures in plant operation, it was assumed that fifty pipe diameters distance between the point of injection of the diluent and the point of drawing the sample would be necessary in order to ensure thorough mixing. This is probably a greater distance than necessary, since velocities in commercial transfer lines are usually high and consequently there is considerable turbulence. It is certain that if an orifice is installed in the line, complete mixing may be obtained in very much shorter distances. However, it was considered better to assume too great a distance rather than too short a one. On the basis of this assumption the diluent will seldom be subjected to high temperature for more than 2 seconds.

The stability of the naphthenic acids under these conditions was determined in the laboratory by passing a stream of recycle gas oil through a heater, introducing a stream of naphthenic acids at the heater outlet, and cooling and collecting the combined streams after they had been kept in contact for the desired length of time. The rates of flow of both the gas oil and naphthenic acids were accurately measured and the acid value of the combined sample was determined. In these runs only one determination of the acid value was made on each sample. The results obtained at various temperatures and times of contact corrected for a blank determination on the gas oil alone are tabulated in Table IV.

TABLE IV. STABILITY OF NAPHTHENIC ACID

Heater Outlet ° C.	° F.	Pressure Lb./sq. in.	Time of Contact Sec.	Naphthenic Acid in Product	
				Calcd. %	By analysis %
426.67	800	400	1.74	1.23	1.24
465.56	870	400	2.51	1.47	1.45
465.56	870	400	10.00	1.40	1.42
465.56	870	400	17.50	2.53	2.49

It is apparent from these data that naphthenic acids or at any rate the acid radical of the naphthenic acids is sufficiently stable at hot-oil recirculating line conditions to permit its use.

Coking Tendencies

The possibility of coking tendencies of the naphthenic acids should be considered when the method is used on superclean recirculating streams. In view of the small quantity of diluent involved and the short time during which it would be introduced, it is not probable that it would noticeably accelerate coking of the heaters. If difficulty with coking is experienced naphthenic acids of higher acid value may be used. Naphthenic acids of higher acid value should have less tendency to cause coking, because of a lower distillation range and also because the amount required for an accurate measurement of oil rate would be less.

Plant-Scale Test

As a further check on the dilution method using naphthenic acids as the diluent, several test runs were made on a commercial cracking unit comparing fresh charge rates determined by the dilution method with tank gagings. It was not possible to check the method on a hot-oil recirculating stream since, as pointed out earlier, this would have required cooling and reheating of the stream to permit gaging. However, since the stability of naphthenic acids at high temperatures had already been established, it was believed that the test runs on the cold-oil streams would be adequate to establish the usefulness of the method.

The charge stock in these tests was a viscous reduced crude which necessitated using the electrometric method of titration for determination of acid value of the mixed stream. The naphthenic acids were injected into the charge line at a

constant rate with a small chemical proportioning pump, and the rate of injection was determined by measurements on a small calibrated tank using a hook gage. The diluent was introduced into the charge pump suction line and the mixed stream was sampled in the pump discharge line. Samples were taken at equal intervals over a 30- to 40-minute period and were composited for analysis. Two tests were made at different times, one with a diluent rate equal to 2.7 per cent of the charge rate, the other with a diluent rate which was 4.3 per cent of the charge rate. The charge rates calculated from these tests were 101.6 and 102.3 barrels per hour, respectively, compared with 103.3 barrels per hour determined by tank gaging for both periods. This agreement is considered entirely satisfactory.

Conclusions

The results of this investigation indicate that naphthenic acids will fulfill all the requirements for a satisfactory diluent in measuring the rates of flow of hot-oil streams by the dilution method. It is noncorrosive, and will not injure the products from the equipment. It is sufficiently stable at the conditions encountered and its concentration may be determined with satisfactory accuracy and rapidity. As pointed out above, the dilution method is not intended for continuous use but only for short tests or calibrations. Under these conditions the cost of the naphthenic acid for use as the diluent should be moderate. For example, using a diluent concentration of 1 per cent, a 20-minute check could be made on a transfer line handling 300 barrels of oil per hour, with a consumption of only one barrel of naphthenic acid.

The cost of the necessary equipment is also moderate. The only changes to existing piping required are the installation of connections for injection of the diluent and for withdrawal of the sample. These two connections should be separated by a distance sufficient to ensure thorough mixing of the diluent, but should not be far enough apart to subject the naphthenic acid to high temperature for an excessive length of time. Equipment is also required for measuring and injecting the naphthenic acid. An accurately calibrated charge drum and a proportioning pump are entirely suitable.

The dilution method of measurement using naphthenic acids has been used on a commercial cracking unit and appears to be a simple and accurate test procedure for the determination of hot-oil flow rate.

Acknowledgment

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Plasticity of Coals

Its Measurement and Relation to Quality of Coke Produced

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Determinations of plastic properties of bituminous coking coals by revised Davis plastometer, Agde-Damm, and Layng-Hathorne test methods show closer correlation of data than has been obtained heretofore. It is shown that definite form of apparatus and procedure of test are important governing factors in this better duplicability of results.

The comparative merits and limitations of data from each revised method are discussed. It is concluded that the most complete and reliable information upon the plastic properties of bituminous coking coals is given by the modified Agde-Damm test for the preplastic range and by the modified Davis plastometer for the plastic range. The modified Layng-Hathorne test, while showing some improvement over the older procedure, is less satisfactory because of uncontrollable variables.

Plasticity data from the revised Agde-Damm and plastometer tests enable a fairly reliable prediction of the strength of a coke to be expected from the carbonization of a bituminous coking coal.

BITUMINOUS coking coals, when heated at a moderate rate in the absence of air, undergo complex and continuous changes in chemical composition and physical character. During carbonization, most bituminous coals, except those bordering on the lignites and semianthracites, show evidence of softening, coalescence, swelling, fluidity, and finally hardening of the coal substance. There are marked distinctions in the degree to which each of these plastic characteristics is shown by different bituminous coking coals. Even for a given coal, the magnitude of these observations is affected greatly by the particular conditions under which such properties are determined. Moreover, complete interpretation of observed plasticity data is complicated by the transient character of the chemical and physical changes involved. Direct applications of plasticity data as absolute indices of the behavior of a coal in gasification, in coke-making, or in combustion are, therefore, made difficult. The aggregate information gained from laboratory tests, however, when certain related temperature, pressure, and expansion (or contraction) data are combined and suitably weighed, furnishes a valuable guide for more complete interpretations of the probable nature of the mechanisms of softening, fusion, coalescence, solidification, and accompanying phenomena.

In the Bureau of Mines survey of the gas- and coke-making properties of coal the plastic properties of bituminous coals have been determined from measurements of viscosity, of expansion and contraction, and of resistance to flow of an inert

gas, observed during the heating of the coal charge under controlled conditions. The literature is replete with references to and publications upon methods of measuring the plastic properties of bituminous coals. No attempt will be made here to give a complete bibliography. Original publications upon the better-known test methods, some later important applications of these and modified procedures for measuring plasticity and related properties of coals, and certain interpretations of the significance of plasticity characteristics in explaining the behavior of a coal on heating have appeared (1, 4-9, 16-26). It seems desirable here to deviate from the usual orthodox classifications of test methods according to the type of apparatus employed or the names of the investigators and follow instead a classification based upon the properties of the coal.

Methods for Measuring Plastic Properties of Coals

Penetrometer instruments in which a needle moves vertically or laterally through the heated coal mass, apparatus measuring resistance to shear caused by movement of a stirring device within the coal, and extrusion instruments depend on changes in viscosity to characterize the plastic properties of coal. Dilatometer methods, which measure the linear expansion or contraction of a test sample, frequently under a known load, have been widely used to define the plastic properties from swelling and softening observations on the heated coal. The gas-flow principle, which depends on variations in the void spaces of the test sample during heating through the plastic stage, has also been widely applied.

The principles of the three distinct methods just cited for measuring the plastic properties of bituminous coals have been extensively applied in the Davis plastometer, Agde-Damm, and Layng-Hathorne test methods, respectively. These methods with some changes in the two latter tests (11, 12) were used in the Bureau of Mines laboratory on the first thirty-two coals (11, 13, 15) tested in the Bureau of Mines-American Gas Association survey of American coals. Comparison of the plasticity temperature and pressure data found on these coals frequently showed poor correlation between these test methods on certain coals. The objects of the present study were to determine as far as possible the reasons for this lack of agreement, to revise the operating technic in each test so as to obtain better correlation of data, and to apply the new data in a practical prediction of coke quality. The three test methods as now employed in the Bureau of Mines laboratory are described below.

MODIFIED DAVIS PLASTOMETER TEST. This test method as now used makes a continuous measurement of the viscosity of the coal while it is heated through the plastic state. Figure 1 shows a vertical section through the instrument.

The technic now used in making a test is to charge 18 grams of 0- to 20-mesh coal into the retort, which is then assembled by screwing in place the head containing the thermocouple well. The retort is placed in the furnace and rotated continuously at constant speed (2 r. p. m.) by means of a motor-driven chain attached to the sprocket on the outer shaft. The resistance, or torque, necessary to prevent rotation of the inner shaft, caused by the coal charge moving against the rabble arms, is measured by the position of the indicating dial. The scale is calibrated in kilogram-centimeters (inch-pounds, or more properly, pound-inches) directly with weights. Free rotation of the dial is pre-

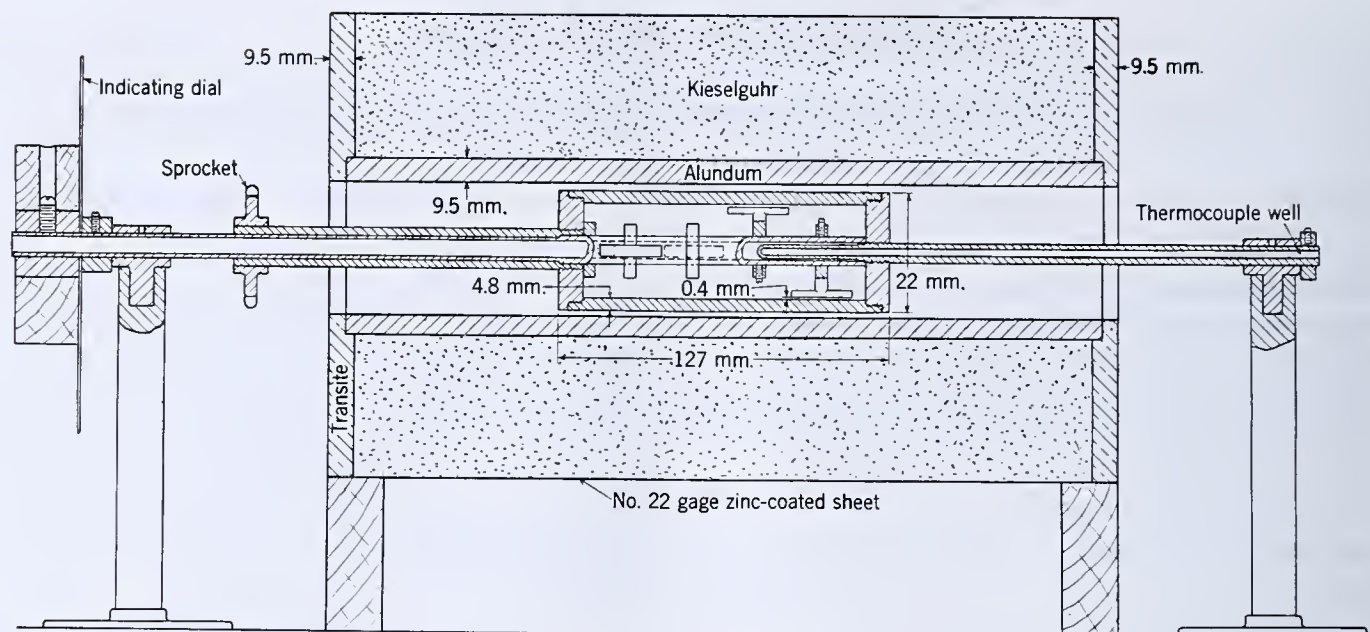


FIGURE 1. PLASTOMETER

vented by means of tension springs not shown in Figure 1. The coal charge is heated at a rate of $4.8^\circ \pm 0.2^\circ \text{C.}$ per minute. Temperatures and resistances are observed and recorded at 2- to 5-minute intervals within the plastic temperature range. "True" temperatures of the coal are obtained by adding experimentally predetermined corrections found from temperature measurements taken in the center of the retort to those temperatures observed regularly in the thermocouple well.

When the temperature reaches the plastic range, the coal sample becomes viscous, and resistance to rotation develops rapidly. With higher temperatures the resistance usually decreases because the coal becomes more fluid. As the heating is continued further, chemical changes in the coal cause it to become more and more viscous and finally to solidify. When solidification occurs the coke formed is quickly broken up and resistance to rotation practically ceases, thus indicating the end of the plastic range.

MODIFIED AGDE-DAMM TEST. This "expansion test" indicates the plastic properties of a coal by measuring the linear expansion and contraction which a small cylindrical briquet of coal undergoes while being heated to 500°C. Figure 2 shows a vertical section of the assembled apparatus ready for the test.

Two coal briquets are formed by compressing 0.7-gram samples of 0- to 60-mesh coal in 7.6-cm. glass test tubes of 0.8-cm. bore at 10.3 kg. per sq. cm. (146 lb. per sq. inch). The lengths of the finished briquets (approximately 1.8 cm.) are then carefully measured and the tubes inserted in the 1.1-cm. holes of the copper heating block. One briquet is allowed to expand freely during the test. The second briquet supports a total weight of 500 grams, represented by the assembly shown in Figure 2. The micrometer distance gage is set arbitrarily to register the measured length of this coal column. The changes in length of the column during a test are indicated directly by the gage readings.

The coal charge is heated at a rate of $4.8^\circ \pm 0.2^\circ \text{C.}$ per minute. Temperatures are measured by thermocouples in the hollow-rod plunger and copper block. Gage and temperature readings are taken and recorded at 5-minute intervals up to 270°C. and at 2-minute intervals thereafter, until the end of the run at 500°C. It is usually advisable to take additional readings at 1-minute intervals near the critical temperature points (where the change on the distance gage is from contraction to expansion, or vice versa) and elsewhere in the test where the rate of gage movement is rapid. A small electric buzzer is used to tap the gage before each reading, except when the rate of change is quite rapid.

Two predetermined sets of corrections are applied to eliminate the effect of the thermal expansion of the instrument and to obtain the "true" coal temperatures. Corrections for the thermal expansion of the instrument from room temperature

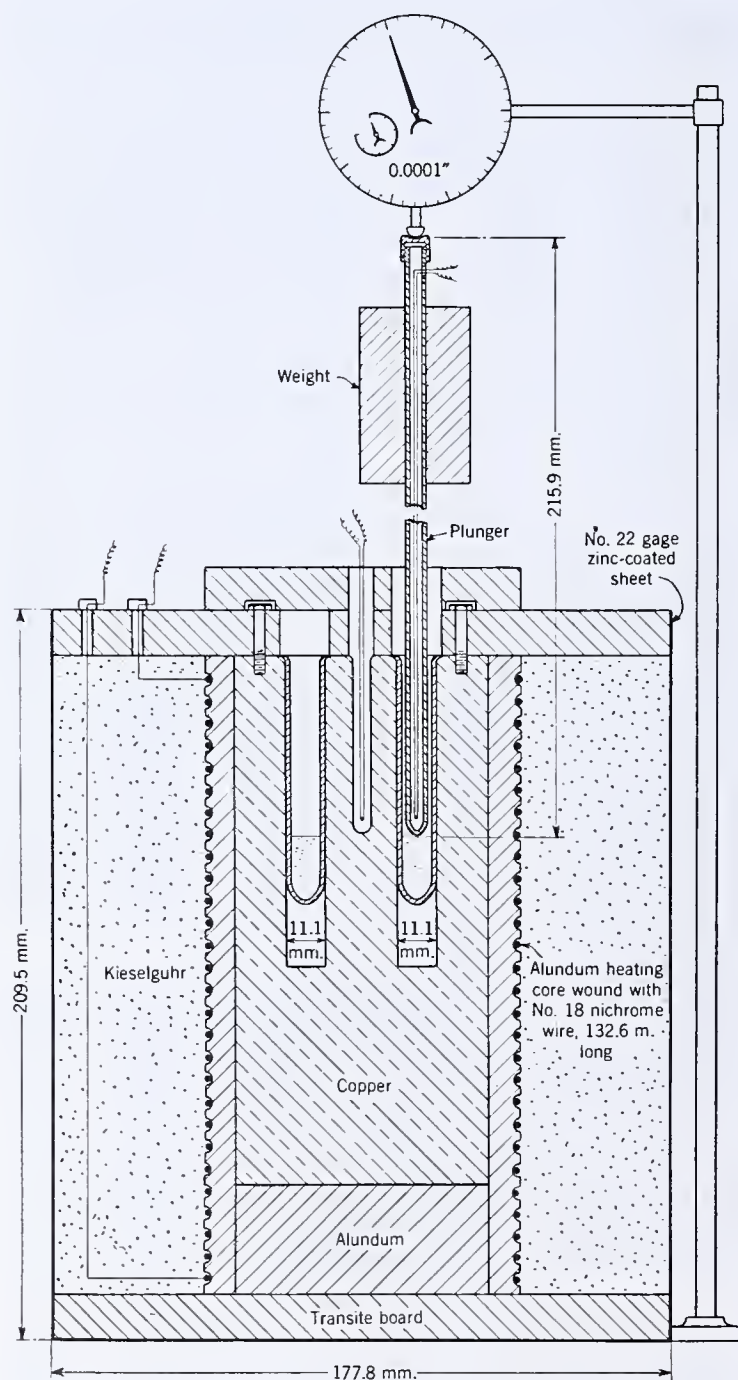


FIGURE 2. MODIFIED AGDE-DAMM APPARATUS

TABLE I. SUMMARY OF PLASTIC RANGE TESTS

Coal	Coal Bed	Modified Agde-Damm											Modified Layng-Hathorne			
		Dry Mineral-Matter-Free Fixed Carbon %	Initial contraction ° C.	Initial expansion ° C.	Free expansion swelling coefficient	Resistance development ° C.	Modified Davis Plastometer								Plastic range ° C.	Maximum resistance, mm. water
							Maximum fluidity			Maximum resistance			Resistance ends ° C.			
						° C.	Kg.-cm.	In.-lb.	° C.	Kg.-cm.	In.-lb.	° C.		° C.		
28	Pittsburgh	62.6	315	391	2.4	
35	{ 70% coal 28 30% coal 33	62.0	326	409	1.0	403	1.6	(1.4)	431	21.2	(18.4)	470	475	391-435	122	
33	Millers Creek	60.1	360	Above 490	1.0				No resistance					None	37	
34	{ 70% coal 33 30% coal 23	65.1	372	Above 500	1.0				Slight intermittent resistance					None	31	
23	Pocahontas No. 4	84.2	439	Above 500	1.0				Slight intermittent resistance					
36	Alma	62.4	312	409	1.7	403	0.2	(0.2)	434	30.0	(26.0)	464	490	384-431	195	
37	{ 80% coal 36 20% coal 23	66.6	335	419	1.0	416	1.2	(1.0)	437	30.0	(26.0)	467	490	385-432	143	
38	{ 70% coal 36 30% coal 23	68.4	346	425	1.0	421	0.5	(0.4)	435	39.2	(34.0)	485	494	379-434	169	
39	Upper Cedar Grove	60.9	308	405	1.2	406	0.9	(0.8)	440	46.1	(40.0)	479	490	395-444	88	
39A	{ 80% coal 39 20% coal 41	65.3	331	418	1.0	417	0.9	(0.8)	439	94.5	(82.0)	483	489	384-448	106	
39B	{ 70% coal 39 30% coal 41	67.4	340	418	1.1	420	1.6	(1.4)	440	94.5	(82.0)	485	491	383-447	116	
41	Beckley	81.3	410	454	1.0	447	2.1	(1.8)	469	82.9	(72.0)	503	515	445-525	190	
40	Lower Cedar Grove	62.7	334	413	1.3	415	0.6	(0.5)	440	47.2	(41.0)	467	478	414-447	199	
40A	{ 80% coal 40 20% coal 41	67.1	338	413	1.3	418	1.2	(1.0)	443	66.8	(58.0)	472	487	404-451	178	
40B	{ 70% coal 40 30% coal 41	68.6	344	414	1.3	414	2.3	(2.0)	443	86.4	(75.0)	480	487	400-...	145	

to 500° C. were predetermined from gage readings in blank runs in which a cylindrical block of quartz was substituted for a coal briquet of like dimensions. These readings are subtracted from gage readings at corresponding temperatures observed in regular tests. Temperature measurements made in the center of the coal charge in separate runs gave data to correct the lower plunger and higher block temperatures regularly observed in test runs.

When the charge of coal reaches a temperature of about 300° C., the individual particles soften and rather rapid contraction takes place. As the temperature rises, this contraction continues with increasing rate to the point of initial rapid expansion at which a very sharp change in direction of the expansion-temperature curve is noted. Shortly after rapid expansion occurs, the coal with continued heating frequently becomes so fluid that it will no longer support the weight of the plunger, which may sometimes even sink to the bottom of the test tube. Upon completion of the test at 500° C., the free expansion sample is removed from the furnace, allowed to cool, and its length again measured. The net linear change during the test is expressed as the "swelling coefficient." The significance of the expansion and contraction characteristics shown by the coal under these test conditions will be pointed out in the discussion of results.

MODIFIED LAYNG-HATHORNE TEST. A detailed description of the apparatus and general operating technic have been given in an earlier publication (12). The procedure has been modified to use a 3-cm. column of 0- to 20-mesh coal, supported in the electric furnace and heated under controlled rates as previously described (12). Pressures in the apparatus necessary to force a stream of purified nitrogen at 20 cc. per minute through the charge and corresponding temperatures at the wall of the glass tube opposite the center of the charge are read and recorded at 2- to 5-minute intervals during the test. Predetermined corrections found from temperature measurements taken in the center of the coal charge are subtracted from the observed temperatures to obtain the "true" coal temperatures. When the temperature is reached at which the coal softens, the resistance to gas flow increases markedly until a maximum is reached. The resistance then drops to approximately its initial value. The significance of the resistance-temperature curve obtained in this manner is discussed below.

Coals Tested

The bituminous coals tested in this investigation are current coals under study in the B. M.-A. G. A. survey of American coals. For ready comparison of the plasticity data with the gas-, coke-, and by-product-making properties of these coals, as published (14), or to be published, the coals have been assigned the same numbers. Table I gives the coal number, the name of the coal bed, the per cent of dry, mineral-matter-free fixed carbon designating rank (2), and plasticity data by the three revised test methods. The recorded plasticity data represent averages of repeat tests (two or more) by each method upon each coal. Coals 28 and 23 used in blending coals 33 and 36 were second lots of coals 28 and 23 used earlier in the survey (11). Shortage of sample of coal 28 prevented plasticity determinations by the plastometer and gas-flow methods. Except for coals 23 and 41, the coals and their blends are all of high-volatile A rank.

Discussion of Results

A study of the data summarized in Table I obtained by the three revised test methods shows, in general, much closer agreement on a given coal than was found by these methods as previously employed. The better checks are partly due to the correction of temperature data to obtain the "true" temperature of the test samples. The previous objections to the necessity for preparation of a special 0- to 100-mesh coal sample for the Agde-Damm test and the use of sized fractions of 20- to 40-mesh coal and coal-electrode carbon mixture for the Davis and Layng-Hathorne methods, respectively, have been eliminated by the use of representative 0- to 60- and 0- to 20-mesh coal samples. Slower rotation of the Davis retort gives results in accordance with the known fact that fluidity of a coal must result before pronounced coke formation occurs. The changed procedure—i. e., using a 3-cm. column of 0- to 20-mesh coal without electrode carbon—in the revised Layng-Hathorne test gives somewhat better correlation of data with that found by the other two test methods. The values of the maximum resistances developed, however, in successive tests by this method are still not closely duplicable and the temperature-pressure relationships are not as sharply defined as those shown by the other two tests.

In general, the Davis plastometer gives much more com-

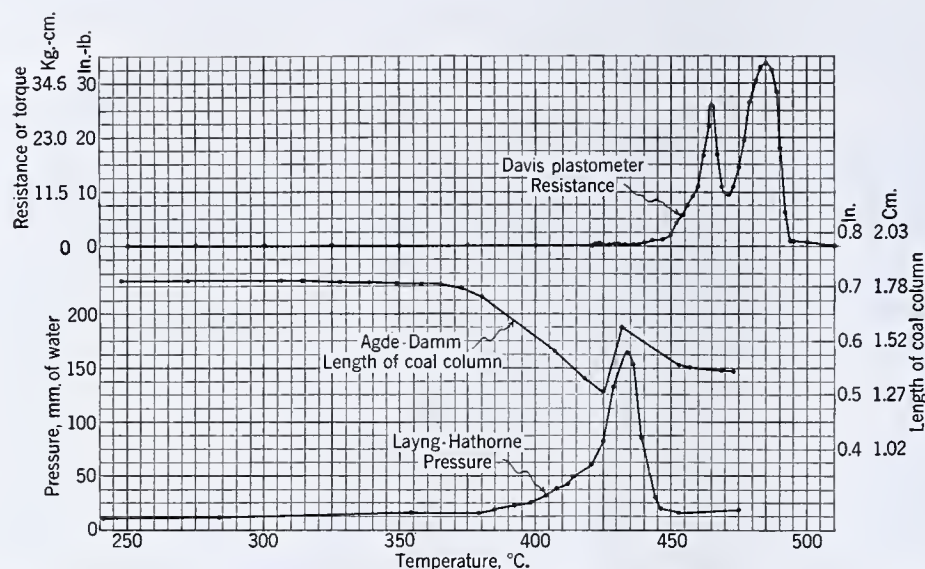


FIGURE 3. PLASTIC PROPERTIES OF BLEND OF 70 PER CENT ALMA AND 30 PER CENT POCAHONTAS COALS

plete information in the plastic range. Minor limitations of this method lie in the difficulties of determining accurately small changes during the period of greatest fluidity and extremely high resistances, above 63.4 kg.-cm. (55 inch-pounds) shown by certain coals. The critical temperature points for such coals in the present work were checked by a smaller, two-rabble-arm retort. Extrapolation of temperature-resistance curves constructed from data by the four-rabble-arm instrument showed excellent agreement in every instance with that predicted from test data by the two-rabble-arm instrument. It is hoped that a stronger drive now planned for the four-rabble-arm retort will eliminate its present minor limitations.

Reference to the data in Table I shows that the Agde-Damm test gives an indication of softening (initial contraction temperature) at a temperature considerably lower than any observed plasticity shown by the other two test methods. Proof that softening and incipient fusion do occur in coal at temperatures considerably below the initial expansion temperatures has been given by Thiessen and Sprunk (27). The temperature at which rapid contraction is observed in the Agde-Damm test is interpreted at that point where the coal particles begin to soften appreciably and the pressure of the plunger presses coal into the void spaces of the charge.

Table I illustrates the very close agreement between "the temperature of initial expansion" in the Agde-Damm apparatus and the temperature where resistance develops in the plastometer. As was pointed out by Audibert and Delmas (3), the swelling or intumescence, as observed here in the Agde-Damm test, is caused by imprisoned gas bubbles and occurs after individual coal particles fuse together and impede the escape of gas. It is also this fusing together of the coal particles that gives rise to the initial resistance to stirring observed in the plastometer test. This has been demonstrated by stopping a plastometer test 5° C. below the point at which initial resistance develops, quenching the retort to room temperature, and removing the coal charge. It was found that only a very slight or incipient state of fusion had resulted in the coal. However, when the test was continued until 10° C. above the initial resistance temperature, the coal had completely fused.

With the foregoing generalizations in mind, a more complete picture of the plastic characteristics of the fifteen coals would be gained by detailed studies of their temperature-pressure

plasticity curves. Lack of space, however, prevents graphic representation of all the data. The characteristic features of the temperature-pressure relationships are, therefore, presented for three typical coals. Figures 3, 4, and 5 are for coals 38, 40, and 41, respectively.

Inspection of the curves shows that shortly after the initial rapid expansion temperature is reached in the Agde-Damm test, a sudden change from expansion to apparent contraction of the coal charge is frequently noted. This reversal takes place at a temperature approximating that of maximum fluidity as observed with the plastometer and is characteristic of all coals showing an appreciable degree of fluidity, as in the case of coals 38 and 40. This sudden contraction is due, in part, to a portion of the coal working out around the plunger, thus leaving less supporting coal substance. Occasionally, a second slight expansion, aided possibly in

part by further action of the fluxing material, is observed. Because of the many uncontrollable variables affecting the movement of the plunger after the temperature of initial rapid expansion, it is evident that much significance cannot be attached to this frequently designated "final expansion temperature" of the Agde-Damm test except, perhaps, for a few less fusible coals.

The plastometer curves show that when fusion of the coal takes place the resistance to stirring increases sharply for a short time and then decreases as the zone of high fluidity is approached. Apparently, this initial rise and fall of the resistance always occur to a greater or less degree. The only explanation the authors can offer for this at present is that evidently the coal when first fused is sticky and contains considerable solid material which imparts a high viscosity to the mass; then when melting becomes more complete, the viscosity is lowered. Following this initial hump portion of the curve, a range of high fluidity is next observed. This may be defined as the distance between the new appearance of low resistance and the change to increasing marked resistance caused by the beginning of solidification. This range of high fluidity is related to the character of the cokes produced, as shown below.

The plastometer curve for coal 38 is unique in the fact that there are two distinct maximum points near the end of the

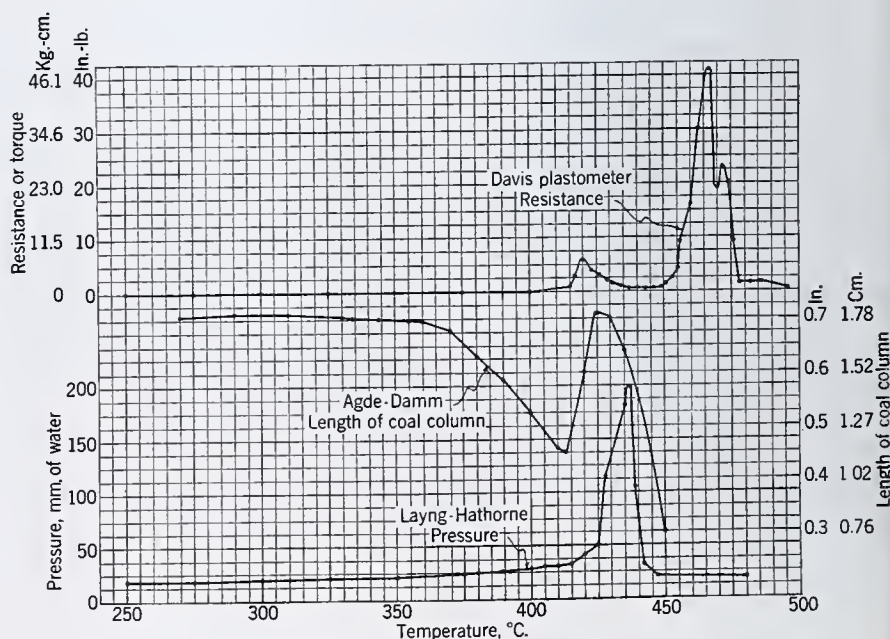


FIGURE 4. PLASTIC PROPERTIES OF LOWER CEDAR GROVE COAL

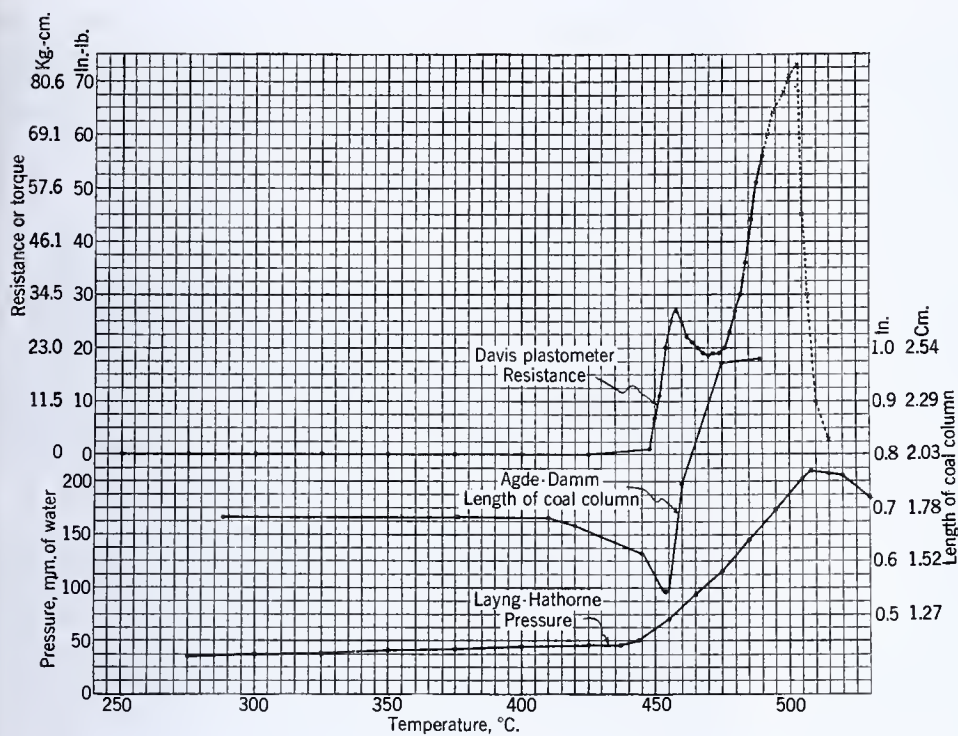


FIGURE 5. PLASTIC PROPERTIES OF BECKLEY COAL

plastic range. This coal consists of a blend and evidently each coal in the blend forms coke more or less separately. From the limited information available at the present time it is thought that these two solidification points indicate a weakening of the coke structure due to the wide difference in the properties of the coals used in this blend. It is well known that the strength of a coke from a blend is dependent upon the character of the entering coals. Weak cokes may result, however, from blends showing only one solidification point.

The Layng-Hathorne curves show that pressure usually starts to develop in this test at temperatures somewhat below the point at which fusion is indicated by the other instruments. Furthermore, the point of maximum resistance in this test may occur approximately where the coal is most fluid, as shown by coals 38 and 40, or may occur elsewhere, as in coal 41. A study of the factors influencing the Layng-Hathorne test showed that both the magnitude of the maximum pressure developed and the temperature at which this occurs are greatly affected by uncontrollable variables in the method. From a study of a large number of Layng-Hathorne curves the authors believe that the test is not capable of giving any reliable information which is not given to a fuller extent by the other tests.

Correlation of Plastic Properties of Coals with Quality of Coke Produced

Table II and Figure 6 show certain general relations between plasticity data on eleven of the coals and the strength of their cokes. The coals have been arranged in the table in the order of increasing average cumulative percentages of their 45.7-cm. (18-inch) retort, 900° C. cokes retained on a 3.81-cm. (1.5-inch) screen in the shatter test and on a 2.54-cm. (1-inch) screen in the tumbler test. These averages for the shatter-tumbler tests will, hereafter, be referred to as the "shatter-tumbler indices." Because of lack of numerical data for the plastic properties of the slightly fusing and non-fusing coals 34, 23, and 33 and for coal 28 used for blending, these coals were omitted from Table II. The relation of plastic properties of these coals to the strength of their cokes will be discussed in connection with coals 35, 36, 37, and 38.

A study of the data in Table II, graphically presented in Figure 6, shows the following general relations: The coke strength increases with (1) decrease in the contraction inter-

val temperature range (the difference between initial expansion and initial contraction temperatures obtained by the modified Agde-Damm test); (2) decrease in the plastometer plastic range; and (3) decrease in length of the plastometer high fluidity temperature range. The first two of these general relationships were pointed out by Davis and co-workers (10) who suggested that "a long contraction interval connotes poor coking power" and that "both high-rank, strongly coking coals and low-rank, weakly coking coals have short plastic ranges and that the ranges of coals lying in between tend to increase with coking power." The present paper does not include a sufficiently large number of high-rank and low-rank coking coals to prove conclusively this second relationship. The evidence in Table II and Figure 6, taken in conjunction with the following discussion of coals 33, 28, 34, and 23, however, strongly supports the statement that the strength of the coke produced increases with decrease in the length of the plastic range as determined by the plastometer.

The relative ranks of the fifteen coals may be obtained by comparing their percentage of dry, mineral-matter-free fixed carbon recorded in Table I.

It will be seen that coal 33 is a low-ranking high-volatile A coal. When blended with 70 per cent of coal 28 (a high-ranking high-volatile A coal) it should give in coal 35 a coal capable of producing a stronger coke. This was found to be the case. Coal 33 has a "shatter-tumbler index" of 47.25, while coal 35 shows 64.25. Likewise, a stronger coke should be produced from coal 34 (a blend of 70 per cent of coal 33 and 30 per cent of coal 23, a high-ranking low-volatile coal) than from coal 33 alone. The "shatter-tumbler index" on coal 34 is 65.7. Coal 36 and its blends, coal 37 (a blend of 80 per cent of coal 36 and 20 per cent of coal 23), and coal 38 (a blend of 70 per cent of coal 36 and 30 per cent of coal 23) show some interesting relations. The respective "shatter-tumbler indices" are 56.85, 69.2, and 64.3.

At first thought one might expect that the coke from coal 38 would be stronger than that from coal 37. More complete study of the data in Tables I and II, however, shows coal 23 to have (1) a dry, mineral-matter-free fixed-carbon content of 84.2 per cent (near the upper limit for bituminous coals), (2) an extremely high "initial contraction temperature" and no "initial expansion temperature" under 500° C. by the Agde-Damm test, and (3) nearly negligible resistance by the Davis plastometer. Reference to the Davis plastometer temperature-resistance curve for coal 38, Figure 3, illustrates rather strikingly that one may here be dealing with what amounts to two quite different coals instead of a homogeneous blend. The two definite maximum resistances 30.0 and 39.2 kg.-cm. (26 and 34 inch-pound) at 465° and 485° C., respectively, and the character of the curve between these points suggest that, during coke formation, coal 36

TABLE II. RELATIONS OF PLASTICITY DATA TO COKE STRENGTH

Coal No.	Coke Tests, 45.7-Cm. Retort, Cumulative % at 900° C.			Modified Agde-Damm, Initial Contraction Interval ° C.	Modified Davis Plastometer	
	Shatter indices	Tumbler indices	Shatter-tumbler indices, average	Plastic range ° C.	High fluidity range ° C.	
36	60.3	53.4	56.85	97	87	19
39	70.7	49.1	59.9	97	84	15
39A	71.0	56.4	63.7	87	72	14
35	70.5	58.0	64.25	83	72	12
38	68.8	59.8	64.3	79	73	12
40	71.6	57.2	64.4	79	63	11
37	75.7	62.7	69.2	84	74	7
39B	79.6	60.3	69.95	78	71	6
40B	76.3	64.0	70.15	70	73	4
40A	77.3	63.7	70.5	75	69	3
41	82.1	66.7	74.4	44	68	1

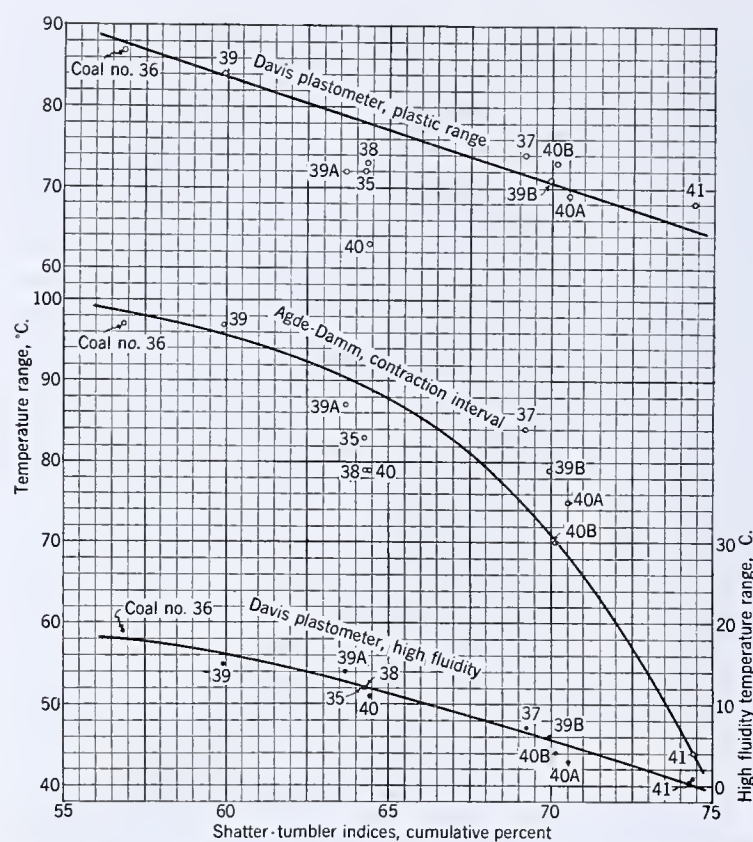


FIGURE 6. RELATION OF PLASTIC PROPERTY TEMPERATURE CHARACTERISTICS OF COAL TO STRENGTH OF COKE

had almost completely coked before coal 23 had started. The net result was the production of a coke of weaker structure from coal 38 (the 70:30 blend) than from coal 37 (the 80:20 blend). The value of the maximum resistances, 30.0 kg.-cm. (26 inch-pound) for coals 36 and 37, and the tendency toward the formation of a second maximum of 9.2 kg.-cm. (8 inch-pound) at 475° C. by coal 37 adds support to the above interpretations for coal 38. Apparently, then, coal 38, the blend of 70 per cent of coal 36 and 30 per cent of coal 23, has so much of this latter slightly fusing coal that the resulting coke is somewhat weaker than coke formed from coal 37, the 80:20 blend of these same coals.

Reference to Table II and Figure 6 would suggest that the relation between the Davis plastic range on coal 40 and the "shatter-tumbler index" of its coke is out of line with that for coals of nearly similar properties. Table I shows also that, of all the coals studied, this coal develops the highest maximum resistance by the modified Layng-Hathorne method. However, the temperature range data for this coal as observed by "the contraction interval" in the Agde-Damm test and by "high fluidity" in the plastometer method show good correlations with the "shatter-tumbler index" of the coke produced. It may be pointed out that the yield of coke was lower and the yield of tar higher at 900° C. on coal 40 than would be expected upon comparing these yields with those for coals immediately above and below it in Table II. Furthermore, as may be seen in Figure 4, the evidence of a second maximum in the temperature-pressure curve would indicate a second fusion caused perhaps by a portion of the tar being released at about 470° C. These peculiarities for coal 40 may explain in part the lower plastic range than would be expected upon comparison with coals of similar composition. The other coals in Table II show no important exceptions in the general correlations between coke strength and plastic properties.

Summary and Conclusions

Critical studies of the apparatus and procedures formerly used in the Agde-Damm, Davis plastometer, and Layng-

Hathorne tests have resulted in the development of improved methods for measuring the plastic properties of coking coals. Test results by the revised methods show better agreement and afford more complete information of the relationships of plasticity to other properties of coals and their cokes than has been possible heretofore. It is concluded from this study that plasticity measurements by the Davis plastometer method as now modified give more reliable and complete information over the plastic range than can be obtained by the other two methods. Data from the modified Agde-Damm test method provide valuable knowledge on the preplastic temperature range, but have limited significance, except for the less fusible coals, in the plastic range. Measurements of plasticity by the modified Layng-Hathorne method, while showing some improvements, furnish but little reliable information that cannot be more accurately and completely provided by the Davis plastometer method.

The quality of coke produced is predictable with a fair degree of certainty from the plasticity data on the coal carbonized. The strength of the coke has been shown to increase with decreases, in the Agde-Damm "contraction interval," in the length of the "plastic range" and the length of "high fluidity" as observed with the Davis plastometer.

Acknowledgment

The authors are indebted to J. D. Davis and A. C. Fieldner for many helpful suggestions during the course of the work. Acknowledgment is made to H. M. Cooper for the analyses of the coals from which the dry, mineral-matter-free fixed carbon designating the ranks of the coal were calculated.

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Hexanitrate Ammonium Cerate as a Proposed Reference Standard in Oxidimetry

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CERIC sulfate has been generally accepted as a volumetric oxidation reagent comparing favorably with potassium permanganate in versatility, accuracy, and convenience. Many of its characteristics make it a preferred reagent by comparison with permanganate. New developments in high-potential, reversible, internal indicators having suitable color transitions, when used in connection with ceric sulfate oxidations, have eliminated the unfavorable comparison with self-indicating permanganate reactions. The commercial availability of the double salt, ceric ammonium sulfate, $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, which is easily soluble in dilute sulfuric acid, has eliminated the unfavorable necessity of preparing ceric sulfate solutions from relatively impure samples of ceric oxide. The notable stability of ceric sulfate solutions, during storage under ordinary conditions and in the case of hot solutions, is a favorable circumstance in comparison to permanganate.

It would appear that the most appropriate advance in the study of new developments in ceric salt oxidimetry still to be made is that of providing a salt suitable for use as a standard of reference. This problem at first thought might be considered almost impossible of solution. The known difficulty associated with the separation of cerium from its associated rare earth elements, praseodymium, neodymium, and lanthanum as well as thorium, has been too often experienced. Attempts have been made to utilize the double salt, ceric ammonium sulfate, as the basis of a product suitable as a standard of reference. The influence of varying concentrations of sulfuric acid and ammonium sulfate upon solutions of ceric sulfate in the attempt to prepare a double sulfate of cerium with ammonium of definite composition greatly complicates the problem. The ceric oxide or oxalate suitable in such a synthesis would have to be of high purity and therefore inaccessible. A double salt is inherently objectionable for obvious reasons of variable composition. The double ceric ammonium sulfate also is hydrated and its equivalent weight so high that a reference standard based upon its use would, if one succeeded in its preparation, be prohibitive in cost.

Advantages in Use of Complex Nitrate Cerate

1. Hexanitrate ammonium cerate is a complex salt as distinguished from a double salt (with possible variations in combining proportions) and is of high equivalent weight (548.258). The salt is not noticeably hygroscopic under ordinary atmospheric conditions. The secondary ionization of the $\text{Ce}(\text{NO}_3)_6^{--}$ ion to form ceric and nitrate ions is not pronounced but is ample for the purpose of the oxidation of divalent iron (and probably other reducing agents) as well as for the oxidation of suitable indicators and for potentiometric end-point phenomena. The product is commercially available at reasonable cost.

2. A product 99.5 per cent pure can be easily prepared by one crystallization starting with a low-grade (40 to 50 per cent) thorium-free mixture of ceric oxide containing lanthanum, praseodymium, and neodymium. A second crystallization of hexanitrate ammonium cerate from concentrated nitric acid in the presence of excess ammonium nitrate results in an 80 per cent yield of product of practically perfect purity.

3. The newly proposed standard of reference is easily soluble in dilute sulfuric acid, forming a solution which is stable upon storage under ordinary conditions and is perfectly stable upon digestion at 100° C. The crystalline salt is stable at 110° C. and is easily freed from excess nitric acid and ammonium nitrate in contact with which it is prepared. Hexanitrate ammonium cerate is soluble in water (without hydrolysis) as well as in sulfuric, nitric, perchloric, and hydrochloric acids. Pure salts of ceric sulfate and cerous chloride are easily prepared from it by digestion with sulfuric and hydrochloric acids in excess.

Factors Indicating Complex Salt Composition

It is not within the scope of this paper to prove by physical chemical means the belief that hexanitrate ammonium cerate is a complex salt and not a double salt such as ceric ammonium sulfate. That $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ is ionized in solution to form ammonium ions and nitrate ceric ions, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 \rightleftharpoons 2\text{NH}_4^+ + \text{Ce}(\text{NO}_3)_6^{--}$, is, however, clearly indicated. Thus, a solution of the pure acid-free salt in water is not hydrolyzed to form insoluble ceric salts as are the double salt ceric ammonium sulfate and other ceric salts. Solutions of the complex nitrate ammonium cerate in nitric acid are salted out by the addition of excess ammonium nitrate introducing the common ion $(\text{NH}_4)^+$, but are not similarly salted out using excess nitric acid as a result of the addition of the common ion $(\text{NO}_3)^-$. Clear solutions of the complex salt in water can be made which are more than 2.5 N, with color production about equal to 0.1 N ceric ammonium sulfate in normal sulfuric acid.

A nitric acid solution of the nitrate cerate is noticeably slow in oxidizing reaction at the equivalence point when reduced by ferrous sulfate. The remarkably clean separation of the nitrate cerate from solutions containing equal concentrations of the other cerium group metals, except thorium, indicates a distinctly different composition since the other cerium group metals are known to form double salts as distinguished from complex salts. Lastly, the recrystallization of the nitrate cerate from concentrated nitric acid solutions by evaporation gives a product which tends towards a high ceric equivalency. This condition would be interpreted to indicate an impurity of $\text{H}_2\text{Ce}(\text{NO}_3)_6$ in the salt $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. This tendency is eliminated by precipitation in the presence of excess ammonium nitrate.

Preparation of Hexanitrate Ammonium Cerate

A chocolate-brown ceric oxide containing approximately 46 per cent of cerium oxides was used as starting material. It contained approximately 40 per cent ceric oxide and was free from iron and manganese. This product dissolved completely in hot, concentrated nitric acid leaving a residue of foreign material, evidently oxide scale from metal trays used in its ignition during preparation. The concentrated nitric acid solution of the sample was diluted with an equal volume of water, the clear solution decanted from the insoluble foreign material, and the ceric-ion value determined. The theoretical quantity of ammonium nitrate was then added and the solution concentrated to cause the separation of the orange-colored crystals of nitrate cerate. The crystals thus obtained were separated from the mother liquor centrifugally and dried at 100° C. until practically all excess nitric acid was removed. The results of a series of fractional crystallizations following this scheme are given in Table I. The necessity of using a thorium-free starting material is stressed by Cuttica and Tocchi (1).

The two first crops of crystals were combined and 50- to 100-gram portions dissolved in boiling hot, concentrated nitric acid using 270 ml. of the concentrated acid for each 100 grams of salt taken. Ammonium nitrate in amounts between 10 and 30 per cent of the total weight of the salt recrystallized

was then dissolved in the solution, which was cooled in ice water, centrifuged, and dried 1.5 hours at 110° C. The purity of the product thus obtained was determined by dissolving samples in 100 ml. of 1 to 10 dilute sulfuric acid and titrating with standard ferrous sulfate using *o*-phenanthroline ferrous complex as indicator. The ferrous sulfate was standardized against standard ceric sulfate solution which had been standardized using Bureau of Standards sodium oxalate as reference. The results are shown in Table II.

From an examination of these data it is observed that in recrystallization from concentrated nitric acid in the presence of from 15 to 30 per cent excess of ammonium nitrate the composition of the resultant product is theoretical within ordinary analytical accuracy. A 10 per cent excess of ammonium nitrate is apparently too low probably because of the formation of $H_2Ce(NO_3)_6$ in small but appreciable amounts. Each of the five preparations was made from a different portion of the two preparations cited in Table I, the first two from the first sample and the last three from the second sample.

Stability of Solutions in Nitric and Sulfuric Acids

Approximately 0.1 *N* solutions of hexanitrate ammonium cerate in 0.5 *N* to 2 *N* nitric and sulfuric acids were digested under a reflux condenser at 100° C. for various periods of time and were then cooled and the ceric-ion value was determined by titration with standard ferrous sulfate. The results are shown in Table III. A sample of 25.00 ml. of the solutions was used in each case and standardized before and after heating for the specified periods.

From an examination of Table III it is observed that approximately 0.1 *N* solutions of the nitrate cerate in 0.5 *N* to 2 *N* sulfuric acid media are stable after digestion at 100° C. over liberal time intervals. Solutions of the nitrate cerate in 1 *N* to 2 *N* nitric acid are stable in the cold but not at 100° C. It will require a more extended time interval to prove the stability of these solutions stored under ordinary conditions over long periods of time. Reasoning by analogy with the stability of ceric ammonium sulfate solutions which have been shown to be stable at the boiling point for several hours and which have likewise been found permanently stable under ordinary storage conditions, the solutions of the nitrate cerate should prove likewise to be permanently stable.

Influence of Nitrate Ion in Determination of Reducing Agents

It is beyond the scope of this paper to test the use of solutions of the nitrate cerate in 0.5 *N* to 1.0 *N* sulfuric acid for all the applications to which ceric sulfate solutions in the same acid have been employed. The nitrate ion has no influence upon the determination of ferrous iron, the most commonly determined element. It is not expected to interfere in most other cases. The value of the proposed new standard need not be in the least minimized by such considerations. From a solution of a known weight of hexanitrate ammonium cerate in excess sulfuric acid, a solution of ceric ammonium sulfate is easily obtained free from nitric acid by the simple process of digestion. All question of the possible undesirable presence of the nitrate ion is thus eliminated.

TABLE I. PREPARATION OF HIGH-GRADE HEXANITRATO AMMONIUM CERATE FROM LOW-GRADE THORIUM-FREE OXIDES

Impure (46%) Oxides Taken	Hexanitrate Ammonium Cerate Obtained						Total Yield Obtained Purity	Theoretical Yield	Total Recovery	
	1st Crop		2nd Crop		3rd Crop					
	Grams	%	Grams	%	Grams	%	Grams	Av. %	Grams	%
1968	1567	99.40	475	98.82	390	90.1	2432	97.7	2540	93.5
3280	2435	99.43

TABLE II. PREPARATION OF PURE HEXANITRATO AMMONIUM CERATE FROM 99.5 % STOCK

No.	(NH ₄) ₂ Ce(NO ₃) ₆ Taken	0.03959 <i>N</i> FeSO ₄ Required	(NH ₄) ₂ Ce(NO ₃) ₆ Found	Purity Found	Error	NH ₄ NO ₃ , Excess
	Grams	Ml.	Grams	%	%	%
1	1.0000	46.20	1.0028	100.28	+0.28	10
2	1.0000	46.15	1.0016	100.16	+0.16	20
0.08085 <i>N</i> FeSO ₄						
3	2.0000	45.08	1.9984	99.92	-0.08	30
4	2.0000	45.12	2.0000	100.00	±0.00	15
5	2.0000	45.12	2.0000	100.00	±0.00	20

TABLE III. STABILITY OF HEXANITRATO AMMONIUM CERATE IN HOT NITRIC AND SULFURIC ACIDS

Type of Solution of (NH ₄) ₂ Ce(NO ₃) ₆ Used	Acid Concen- tration dur- ing Heating	Normality before Heating	Time of Heating at 100° C. Min.	Normality after Heat- ing
Hexanitrate Ammonium Cerate Solutions in 0.5 <i>N</i> and 1.0 <i>N</i> Sulfuric Acid				
Approximately 0.1 <i>N</i> in 0.5 <i>N</i> H ₂ SO ₄	0.5	0.09621	60	0.09618
	1.0	0.09621	30	0.09618
	1.0	0.09621	60	0.09620
	1.5	0.09621	30	0.09624
	1.5	0.09621	60	0.09622
	2.0	0.09621	30	0.09618
Approximately 0.1 <i>N</i> in 0.5 <i>N</i> H ₂ SO ₄	2.0	0.09621	60	0.09622
	1.0	0.09602	180	0.09602
	1.0	0.09552	60	0.09560
	1.5	0.09552	60	0.09553
Approximately 0.1 <i>N</i> in 1.0 <i>N</i> H ₂ SO ₄	2.0	0.09552	60	0.09569
	1.0	0.09552	180	0.09551
Hexanitrate Ammonium Cerate Solutions 1.0 <i>N</i> and 2.0 <i>N</i> Nitric Acid				
Approximately 0.1 <i>N</i> in 1.0 <i>N</i> HNO ₃ ^a	2.0	0.09107	45	0.09043
	3.0	0.09107	45	0.08942
	4.0	0.09107	45	0.08882
Approximately 0.1 <i>N</i> in 2.0 <i>N</i> HNO ₃ ^a	...	0.09236
	...	0.09236
	...	0.09236

^a 48 hours' storage at room temperature between each standardization.

Summary

Conditions have been established for the preparation in pure form of hexanitrate ammonium cerate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, starting with a low-grade thorium-free mixture of 40 to 50 per cent ceric and cerous oxides containing 50 to 60 per cent of mixed oxides of praseodymium, neodymium, and lanthanum.

The properties of this proposed new standard of reference in ceric oxidimetry are discussed and the indications pointing to its complex nature as distinguished from the double salt type of ceric salt, such as ceric ammonium sulfate, are pointed out.

The stability of solutions of the nitrate cerate in 0.5 *N* to 2.0 *N* sulfuric acid at 100° C. has been studied and perfect stability shown.

The many desirable properties possessed by the proposed new standard, which make its use in the new role desirable, are outlined.

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Construction of Glass Helices for Packing Fractionating Columns

A Rapid Mechanical Method

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SINGLE-turn glass helices have been used by several investigators (1, 2, 3, 6) as packing material in laboratory fractionating columns. Up to the present time their use, particularly in large columns, has been limited to some extent by rather slow and tedious methods of construction.

A method for making these helices by hand was first described by Wilson, Parker, and Laughlin (7). A more detailed account of the construction, breaking, and sorting of glass helices has been reported by Roper, Wright, Ruhoff, and Smith (4), who wound glass spirals from 2-mm. Pyrex rod by hand. The fiber diameter was about 0.6 mm., and the outside diameter of the coil 4.4 mm. About 5 cc. of finished product were produced in 1.5 hours, 1 hour of which was required for breaking and sorting. Recently, a partially mechanical method of constructing glass spirals has been described by Young and Jasaitis (8).

The distilling column which has been used in this laboratory has a packed section of 300 cc. It would take about 80 hours to prepare a sufficient number of helices to pack this column by using the technic of Roper and his co-workers, whereas it was accomplished in 15 hours using the method here outlined.

Winding the Spirals

A mechanical device for winding glass spirals similar to those described by Roper was constructed from Meccano parts. The design of this machine was based on that of a device developed by Tapp (5) for winding spirals from quartz fibers. The machine was built to wind directly a glass spiral, with a fiber diameter of about 0.6 mm. and 11 turns per centimeter, from a Pyrex rod 2 mm. in diameter. The fiber for the spiral was drawn from this rod as the spiral was wound on a winding form.

The mechanical device was constructed in two parts: (1) a unit which rotated the winding form at a uniform rate and, at the same time, moved this form in a direction at right angles to the plane of rotation at a uniform speed; (2) a similar unit which fed the rotated glass rod onto the winding form at a uniform rate. The details of construction of these units are clearly shown in Figure 1.

The power plant was a Bodine electric motor, type CR2, equipped with a 595 to 1 reduction gear. The gear (No. 27a, Meccano part number) on the motor shaft revolved at 16 r. p. m.

and meshed with the gear wheel (No. 31) on the horizontal drive shaft, causing the latter to revolve at 28 r. p. m. The pinion (No. 26) on the drive shaft meshed with the centrate wheel (No. 28) which drove the worm gear (No. 32). The worm gear meshed with the pinion (No. 25) on the shaft driving the chain sprocket (No. 96a). The chain, which was fastened at one end, passed under an idler sprocket and then over the driving sprocket. The other end of the chain was fastened to a spring which applied a tension, thus preventing a slipping motion as the drive sprocket meshed with the chain links and carried the carriage forward. The forward motion was at the rate of 1 mm. per revolution of the winding form which rotated at 28 r. p. m.

The glass spirals were wound on a 3.18-mm. (0.125-inch) diameter steel drill rod, which was coupled to the main drive shaft, and passed through a bearing fixed on the end perforated flange plate of the carriage. The free end of the winding form passed through a bearing which was fastened to another perforated flange plate (right of Figure 2), the latter being fixed to the base board. These two bearings served to steady and guide the form during the winding operation. The end of the winding rod was slotted.

The glass spirals were wound from a 2-mm. Pyrex glass rod, fed through a gas-air flame onto the winding form at right angles to it and in the same horizontal plane. The feeding mechanism is shown in Figure 1, the glass rod being clamped in the second carriage in exactly the same position as that occupied by the winding form in the first. The relative positions of the glass-rod feeding device and the carriage bearing the winding form are shown in Figure 2.

The inner cone of the gas-air flame was about 4 cm. high, and the outer tip was placed under the glass rod approximately 0.5 cm. from the winding form. The tip of the inner cone of the

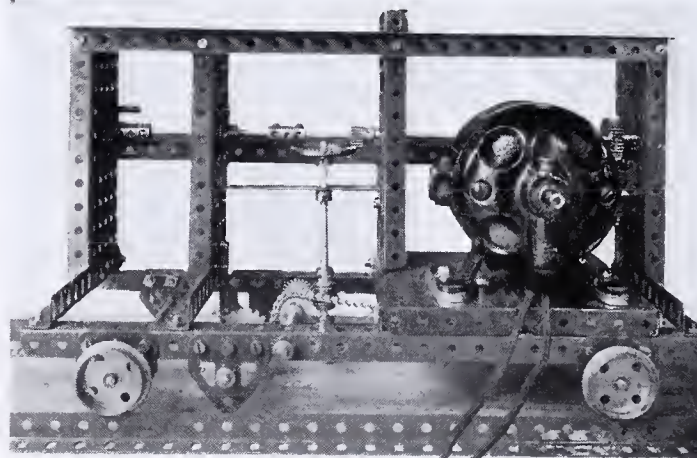


FIGURE 1. GLASS HELIX-WINDING APPARATUS

flame was kept about 0.5 cm. below the Pyrex rod. Variations in the gas or air pressure will cause slight irregularities in the diameter of the spiral fiber. With a little practice, the operator can adjust the flame so that a uniform spiral is produced.

Figure 2 shows a spiral being wound. The original Pyrex rod, the finished spiral, and single-turn helices are shown in Figure 3.



FIGURE 2. GLASS SPIRAL BEING WOUND ON WINDING FORM

To begin winding a spiral, the two carriages were drawn back so that the end of the winding rod and the end of the glass rod almost entered the flame zone. Both motors were started simultaneously with a single switch. As the glass rod passed into the flame and softened, the tip of the rod was drawn out with a short bit of glass tubing, and this fiber was hooked into the slotted end of the winding rod. The finished spiral can be slipped off the free end of the steel winding form when the winding operation is completed.

Preparing the Helices

The method used for cutting single-turn helices from the glass spirals is an improvement on that of any described method that has been noticed by the author. A long spiral was slipped over a 3.18-mm. (0.125-inch) diameter steel drill rod, then held firmly between the thumb and forefinger and each turn nicked by drawing a wedge-shaped pointed Carborundum glass-marking pencil along the top of the spiral. When the etched spiral was squeezed between the thumb and forefinger, each turn broke at the nick. If any turns break less than three-fourths of a turn, they drop off the rod, thereby greatly reducing the period required for sorting. The number of helices breaking between three-fourths of a turn and one turn was very small, and these may be easily and quickly

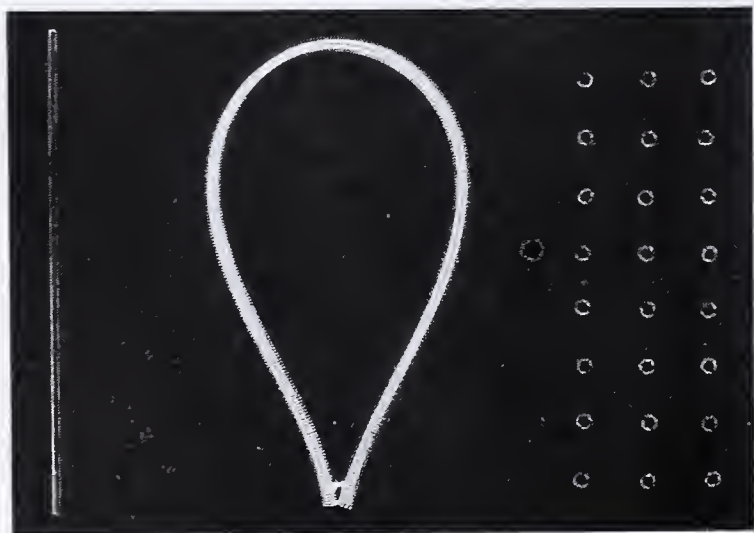


FIGURE 3. ORIGINAL PYREX ROD, FINISHED SPIRAL, AND SINGLE-TURN HELICES

separated as the helices are slipped off the end of the steel drill rod if a uniform packing of exactly one turn is desired. Helices of any required number of turns may be readily made by nicking the spirals at the proper points. The loss due to breakage is low. About 10 cc. were lost in preparing 300 cc. of finished product, as compared with a loss of about 20 per cent with the method of Roper, Wright, Ruhoff, and Smith (4).

The spiral was wound on this machine at the rate of 350 turns per 12.5 minutes. However, with a few simple mechanical changes it is possible to increase the rate of winding considerably, if desired. The finished spiral was about 32 cm. long and had 11 turns per cm. In order to save time, the single-turn helices can be cut from one of these lengths of spiral while another spiral is being wound. Enough single-turn helices to occupy a packed volume of 20 cc. (about 1260), can be made by this method of construction in 1 hour.

Some measurements upon average pieces of the finished product are as follows: fiber diameter, 0.65 ± 0.02 mm.; outside diameter of the coil, 4.47 ± 0.04 mm.; weight of 300 single turns, 2.64 ± 0.04 gram.

The 300 cc. of finished product required to pack the laboratory distilling column were obtained from 32 Pyrex rods 2 mm. in diameter and 92 cm. long.

Table I shows the Meccano parts required for constructing a single carriage for winding the spirals. The total cost of these parts is about \$5.00.

TABLE I. PARTS REQUIRED

No. of Parts Required	Mecanno Part No.	Description
1	6	Perforated strip, 38.1 mm. (1.5 inches)
1	6a	Perforated strip, 50.8 mm. (2 inches)
2	7	Angle girder, 622 mm. (24.5 inches)
4	8	Angle girder, 318 mm. (12.5 inches)
3	9	Angle girder, 63.5 mm. (2.5 inches)
4	12	Angle bracket, 12.7 mm. (0.5 inch)
1	13a	Axle rod, 203 mm. (8 inches)
1	15	Axle rod, 127 mm. (5 inches)
4	14	Axle rod, 165 mm. (6.5 inches)
1	25	Pinion wheel, diameter 19.1 mm. (0.75 inch), 6.4 mm. (0.25 inch) face
1	26	Pinion wheel, diameter 12.7 mm. (0.5 inch), 6.4 mm. (0.25 inch) face
1	27a	Gear wheel, 57 teeth
1	28	Centrate wheel, 25.4 mm. (1 inch) 38 teeth
1	32	Worm
2	37f	Nuts and bolts, 5.6 mm. (0.22 inch)
2	48b	Angle strip, 88.9 mm. (3.5 inches) \times 12.7 mm. (0.5 inch)
7	52	Perforated flange plate, 140 mm. (5.5 inches) \times 63.5 mm. (2.5 inches)
1	96	Sprocket wheel, 25.4-mm. (1-inch) diameter, 18 teeth
1	96a	Sprocket wheel, 19.1-mm. (0.75-inch) diameter, 14 teeth
6	126a	Flat trunnions
1	63	Coupling
10	59	Collar with set screw
4	20	Flanged wheel, 25.6-mm. (1.125 inches) diameter
2 feet	94	Chain

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Direct Determination of Oxygen in Organic Compounds Containing Sulfur

ter Meulen Method

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IN PREVIOUS studies (2, 6, 7) the authors found that, when certain modifications were made, the ter Meulen method (3, 4, 5) for the direct determination of oxygen in organic compounds by catalytic hydrogenation gave satisfactory results. Thus when a very active thoria-promoted nickel catalyst was used, all oxygen was quantitatively converted to water in the analysis of compounds containing only carbon, hydrogen, and oxygen (6), and this was equally true when nitrogen (7) or small amounts of sulfur (2) were also present. The last work (2), which dealt primarily with the direct determination of total oxygen in oils whose sulfur and nitrogen content was below 0.1 per cent, appeared to justify further work with organic sulfur compounds. In an endeavor to make the method more generally applicable, the behavior of compounds containing considerable amounts of sulfur and various types of sulfur linkage has been studied. Even though sulfur is recognized as a serious poison for nickel catalysts, a method has been developed which has given satisfactory successive analyses with the several types of organic sulfur compounds studied.

The Cracking Surface

Cracking surfaces composed of platinized quartz granules, and also of nickelized quartz granules, both with and without thoria, were investigated. While the nickel-coated surfaces appeared slightly more active, they proved unsatisfactory because of large blanks. The platinized quartz cracking surface (6) proved very efficient for most organic sulfur compounds studied. More or less sulfur from the compound was always retained by this cracking surface. Because the aliphatic compounds cracked easily to gaseous products between 600° and 800° C., depositing little carbon, the efficiency of the cracking surface was maintained, and the capacity of the catalyst to resist sulfur poisoning became the limiting factor in determining the number of successive runs possible with one tube-filling. Aromatic compounds which may require cracking temperatures up to 1100° C. deposited considerable carbon which diminished the activity of the cracking surface as successive runs were made. Thus the amount (about 20 cc.) of platinized quartz employed allowed about five successive analyses to be made of either *p*-xylene-sulfonic acid or di-*p*-tolyl sulfoxide, about three of sulfobenzoic anhydride, or about two of diphenyl sulfone.

Failure occurred when the cracking surface was no longer able to prevent easily condensable decomposition products from passing through. A larger amount of cracking surface should make possible an increase in the number of successive analyses of aromatic sulfur compounds. Of the aromatic compounds studied, diphenyl sulfone required the highest temperature for cracking—i. e., about 1100° C.—while for the other aromatics temperatures down to 800° C. sufficed. That the number of successive analyses possible with a given aromatic compound offered a criterion of its cracking characteristics follows from observations that the rate of vaporization of the sample had to be decreased in the above sequence in order to obtain satisfactory cracking. Thus the full extension of the analysis time which has been recommended for organic sulfur compounds was necessary only in the cases of the compounds most difficult to crack.

The Catalyst

Unsupported and quartz-supported nickel catalysts, both unpromoted and thoria-promoted, have been investigated. Ordinarily any of these catalysts entirely sorbed any sulfur compounds not held back by the platinized quartz cracking surface. In fact, hydrogen sulfide was not obtained from any active catalyst under conditions of analysis, or even at 450° C., unless uncracked benzene passed through the system. When this occurred hydrogen sulfide was evolved and the catalyst became completely poisoned. Considerable amounts of sulfur could be present in the system before the catalysts failed in analysis. Thus with aliphatic compounds, in whose analysis the catalyst was the limiting factor, from eight to thirteen runs could be made, thereby introducing some 200 to 400 mg. of sulfur, before the 5 to 10 grams of unsupported promoted catalyst failed to give quantitative conversion of oxygen to water. The smaller nickel content of the supported promoted catalysts allowed about four successive runs on 20 grams of this material.

Certain samples of unsupported catalyst, both unpromoted and thoria-promoted, exhibited a marked and persistent increase in blanks immediately following an analysis—for example, an initial blank of 0.5 mg. per half hour might increase to 2 to 3 mg. directly after a run. However, after passing hydrogen for a few hours, the blanks decreased and finally became constant below their initial values. Observations of this phenomenon led to the belief that hydrogen sulfide was in some way acting upon the catalyst. This contention was strengthened by the results of experiments in which hydrogen sulfide was passed through the tube under the conditions of analysis. In the cases of both promoted and unpromoted catalysts, the blanks were considerably increased thereby. It seems necessary to assume, therefore, that hydrogen sulfide, and perhaps other sulfur compounds which may exist at this stage in the analysis, are capable of accelerating the reduction of nickel oxide which escaped reduction by hydrogen alone during the preparation of the catalyst. Small amounts of such oxide are known to exist within catalyst granules even after prolonged reduction.

It is interesting to note that the increased blanks persisted for some hours after the passage of hydrogen sulfide had been discontinued. This may signify a slow reaction with adsorbed hydrogen sulfide or sulfur, or a specific catalytic effect. Although the phenomenon of increased blanks was not observed when reduction was prolonged for 2 weeks, it was shown by certain samples of unsupported catalyst, among a number which were believed to be identical in composition and mode of preparation, but which were reduced for 24 hours only. Some factor not under control, therefore, appears to have been responsible for a variation in the amounts of residual oxide present in the more rapidly reduced catalysts. A simple and very effective solution of the problem was found to lie in the use of granular quartz-supported nickel catalysts. The nickel was now present only in very thin layers which were readily freed from all but negligible amounts of oxide by reduction in hydrogen overnight at 500° C. It is recommended, therefore, that the supported, promoted nickel be used in all analyses of sulfur compounds as catalyst, but not as cracking surface.

In the analysis of compounds containing only hydrogen, carbon, oxygen, and nitrogen (6, 7) regeneration of the catalyst was possible by oxidizing and then reducing with hydrogen. However, when sulfur was held by the catalyst, oxidation formed nickel sulfate which proved impossible to reduce. Heating the used catalysts to red heat in a stream of hydrogen, without preliminary oxidation, also was unsuccessful because of the slowness of sulfide decomposition and the danger of injuring the quartz tube by contact with melted sulfide. The small amount of trouble and expense involved in replacing a poisoned catalyst with a fresh one is more than offset by the knowledge that a fully active catalyst is in the tube, an especially important consideration when working with new substances.

Apparatus, Materials, and Method

The apparatus used in the major part of the work was essentially that already described (6), with the following exceptions:

To eliminate sources of water within the system, the liquid used in the safety tube and in the flowmeter was purified mineral oil. Either platinized asbestos or reduced nickel was used to remove traces of oxygen from the electrolytic hydrogen employed. By placing the flowmeter before the purification train, it was possible to have the metered hydrogen come into contact only with glass surfaces, except at the short thick rubber connection joining the purification system to the quartz tube. The hydrogen was first dried by calcium chloride and then by Drierite. The Drierite was regenerated in place by an electric furnace heated to 230° to 250° C. Each of the Schwartz tubes in the absorption train also contained Drierite (2). The cracking surface was heated by a heavy-duty electric furnace which was automatically turned on by a simple, improvised, time-power switch.

The unsupported nickel catalysts were prepared as previously described (6), except that final reduction was carried out at 450° C. From 5 to 10 grams of the ignited oxides were used to charge the tube. The supported catalysts were prepared by thoroughly mixing the desired amount of 20-mesh granulated quartz with 5 per cent of its weight of nickel in the form of pure nickel nitrate hexahydrate, and 0.1 per cent of its (quartz) weight of thoria as pure thorium nitrate, dissolved together in just enough hot water to coat the quartz granules uniformly. The mixture was then heated in a casserole over a Bunsen flame until the nitrates were completely decomposed to oxide. About 20 grams of the oxide-coated quartz granules were used to charge the tube. After reduction at 500° C. the granules of quartz were uniformly covered with a very thin deposit of nickel.

The platinized quartz cracking surface was prepared as before (6), while the nickelized cracking surface was prepared in the same manner as the supported catalysts, except that reduction was finally completed at 1000° C.

The method of analysis was in general similar to that described elsewhere (6), except that the rate of hydrogen flow was reduced to 40 cc. per minute, although the catalyst temperature remained at 350° C. The time of analysis may well be extended to 1.5 hours in the case of aromatic sulfur compounds. After reducing the catalysts for 24 hours, the blank on the system was between 0.5 and 1 mg. per half hour. The blank gradually diminished during successive analyses.

Discussion of Results

The results of analyses made by the foregoing method upon high-grade organic chemicals containing sulfur are given in Table I. The accuracy of the analyses is in general better than 1 per cent relative error, which is about the order of accuracy obtained in previous studies (6, 7) of this method.

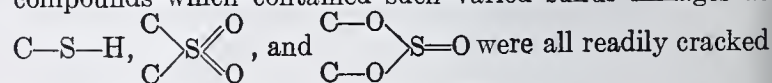
The behavior in analysis of the sulfur compounds studied divided them into two groups—aromatic and aliphatic—primarily on the basis of their cracking characteristics. The number of successive analyses possible with one tube-filling depended in the former group upon the capacity of cracking surface present, and in the latter group, upon the amount of catalyst used. Although the aromatics as a group were more difficult to crack, they showed definite differences among themselves in this respect. Thus these compounds decreased

TABLE I. RESULTS OF ANALYSES BY MODIFIED TER MEULEN METHOD

Substance	Quality	Weight of Sample Gram	Sulfur Calcd. %	Oxygen Found %	Oxygen Calcd. %	Relative Error %
Trional	U. S. P.	0.2103	26.47	26.29	26.43	-0.5
$\text{CH}_3\text{C}(\text{SO}_2\text{C}_2\text{H}_5)_2$		0.1848		26.36		-0.3
		0.1024		26.39		-0.2
		0.1909		26.33		-0.4
$\text{C}_2\text{H}_5\text{C}(\text{SO}_2\text{C}_2\text{H}_5)_2$		0.1147		26.58		+0.6
		0.1228		26.49		+0.2
Ethyl sulfite	Kahlbaum	0.1758	23.21	34.89	34.77	+0.3
$\text{C}_2\text{H}_5\text{O}\text{SO}\text{C}_2\text{H}_5$		0.1184		34.69		-0.2
		0.1168		34.61		-0.5
		0.1219		34.85		+0.2
		0.1040		34.87		+0.3
		0.1130		34.61		-0.5
Thiacetic acid	Eastman highest purity	0.1030	42.14	21.32	21.04	+1.3
CH_3COSH		0.1135		21.09		+0.2
		0.1198		21.07		+0.1
		0.1091		21.18		+0.7
<i>p</i> -Xylenesulfonic acid (dihydrate)	Eastman highest purity ^a	0.1172	14.43	36.06	36.03	+0.1
$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$		0.1143		35.85		-0.5
		0.1020		36.08		+0.1
		0.1035		36.12		+0.3
		0.1189		35.92		-0.3
Di- <i>p</i> -tolyl sulfoxide	Eastman highest purity	0.2626	13.93	6.94	6.96	-0.3
$\text{CH}_3\text{C}_6\text{H}_4\text{SO}\text{C}_6\text{H}_4\text{CH}_3$		0.2682		6.93		-0.4
		0.2689		6.94		-0.3
		0.2222		6.92		-0.6
Sulfobenzoic anhydride	Eastman highest purity	0.1549	17.41	34.83	34.77	+0.2
$\text{C}_6\text{H}_5\text{SO}_2\text{C}_6\text{H}_5$		0.1241		34.81		+0.1
		0.1260		35.13		+1.0
		0.1019		34.98		+0.6
		0.1032		34.63		-0.4
		0.1135		35.05		+0.8
Diphenyl sulfone	Eastman highest purity	0.4063	14.70	14.79	14.68	+0.7
$\text{C}_6\text{H}_5\text{SO}_2\text{C}_6\text{H}_5$		0.4049		14.42		-1.8
		0.3981		14.86		+1.2
		0.3130		14.46		-1.5
		0.3631		14.69		+0.1
		0.3190		14.68		0.0

^a Recrystallized from water.

in ease of cracking in the following order: *p*-xylenesulfonic acid, di-*p*-tolyl sulfoxide, sulfobenzoic anhydride, di-phenyl sulfone. This is the order which would be predicted from the work of Egloff and co-workers (1). This work emphasized the function of side chains in facilitating the cracking of aromatic compounds by furnishing gaseous olefins. In this way the number of methyl groups would explain the relative positions of *p*-xylenesulfonic acid and di-*p*-tolyl sulfoxide, while absence of side chains would account for the end position of diphenyl sulfone. The intermediate position of sulfobenzoic anhydride may be attributed possibly to a direct formation of anthracene, which is known to be more readily decomposed than benzene. On the other hand the fact that the aliphatic compounds which contained such varied sulfur linkages as



and equally satisfactory to analyze, indicates that the type of sulfur linkage is probably not an important factor in determining behavior in analysis.

Conclusion

On the basis of the foregoing work it has been shown that organic sulfur compounds of various types can also be analyzed by the method as modified earlier (6), but it is recommended that a quartz-supported, thoria-promoted nickel catalyst be used.

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Photometric Determination of Silicate in Sea Water

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THE colorimetric method of Dienert and Wandenbulcke (4) is now used universally for the determination of silicate in marine waters. In this method the yellow silicomolybdate complex, which develops quickly in a sulfuric acid solution, is compared with permanent standards prepared from picric acid. The quantity of picric acid in the standards as recommended by Dienert and Wandenbulcke has been shown to be erroneous and more recently has been changed (6, 7). Winkler's method (14), which utilizes a hydrochloric acid solution of molybdate for the reagent and potassium chromate solutions as standards, is recommended by the American Public Health Association (1). Steffens (9) did not think that the reddish yellow color of a potassium chromate solution exactly matches that of the silicomolybdate complex, but Swank and Mellon (11), after completing a spectrophotometric investigation of both picric acid and potassium chromate standards, concluded that potassium chromate standards buffered with sodium tetraborate match very well and are preferable to the picric acid standard. The photometer has been receiving increasing attention in colorimetric analysis because of its great sensitivity, its removal of colors which interfere with the normal visual method, the elimination of color standards, and the ease with which the factors of the method may be studied. Strohecker, Vaubel, and Breitwieser (10) have made a photometric investigation of the Dienert and Wandenbulcke method, using fresh waters. The authors' paper is concerned primarily with the photometric determination of silicate in marine waters.

Preparation of Reagents and Standard Solutions

STANDARD SILICATE SOLUTION. A stock solution was prepared by dissolving 1.421 grams of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (theoretical formula) in silicate-free distilled water, diluting to 2 liters, and storing in a paraffined bottle. The silicon concentration was determined gravimetrically (5), acidimetrically (8), and colorimetrically (7) against picric acid standards. The gravimetric analysis, showing the silicon concentration to be 0.00281 mg. at. of silicon per ml., was considered to be the most accurate. (Milligram atom, abbreviated mg. at., is defined as the milligrams of the element divided by its atomic weight.) The concentration of this stock solution was checked every few days. From this solution was prepared by dilution a standard solution containing 0.000281 mg. at. of silicon per ml.

It has been shown (4, 5) that silicon in the colloidal form is not estimated by the colorimetric method. The fact that the analyses by the acidimetric and colorimetric methods checked the gravimetric analysis indicated that the silicate was in the crystalloidal form.

SYNTHETIC SEA WATER, SILICATE- AND PHOSPHATE-FREE. Synthetic waters of varying chlorinity were prepared by diluting a synthetic water of a chlorinity of 19.00‰. This stock solution was prepared by dissolving per liter 0.7455 gram of potassium chloride, 3.9066 grams of sodium sulfate, 23.38 grams of sodium chloride, 5.000 grams of magnesium chloride, and 1.1097 grams of calcium chloride. Pure potassium chloride, sodium sulfate,

and sodium chloride were weighed directly. Magnesium chloride and calcium chloride were precipitated as carbonates with sodium carbonate and dissolved with a calculated quantity of hydrochloric acid. The previously weighed salts were diluted to a volume of 1 liter. This solution was preserved in a paraffined bottle to prevent silicate contamination from the glass.

STANDARD PHOSPHATE SOLUTION. Pure dry potassium dihydrogen phosphate (4.084 grams) was dissolved in distilled water and diluted to 1 liter. One milliliter contains 0.030 mg. at. of phosphorus. Solutions containing 0.0003 and 0.00003 mg. at. per ml. were prepared by dilution.

AMMONIUM MOLYBDATE REAGENT. Ten grams of c. p. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in 90 ml. of silicate-free distilled water.

SULFURIC ACID SOLUTION. A 6 N solution was prepared from concentrated c. p. acid.

PICRIC ACID STANDARD. Vacuum-dried picric acid (307.5 mg.), recrystallized from benzene (13), was dissolved in distilled water and made to a volume of 1 liter. Fifty milliliters of this solution were diluted to a volume of 1 liter. One milliliter is equivalent to 0.0005 mg. at. of silicon.

POTASSIUM CHROMATE STANDARD. This solution was prepared according to Swank and Mellon (11).

Procedure

PROCEDURE. To a 100-ml. sample of silicate solution are added 4 ml. of ammonium molybdate reagent and 0.5 ml. of 6 N sulfuric acid. After standing 5 minutes the transmission is determined with a Zeiss Pulfrich (gradation) photometer.

Experimental

The measurement of the transmissions of the dilute solutions was determined with a 25-cm. absorption cell; distilled water in a similar cell was the reference standard. A 5-cm. cell, with air as the reference standard, was used with the more concentrated silicate solutions. The recorded transmissions are the averages of the drum readings before and after interchanging the standard and silicate solutions to avoid the possibility of error from unequal illumination. All experimental determinations were made in duplicate at least.

SELECTION OF FILTER. The Zeiss Pulfrich (gradation) photometer is equipped with filters, each having an effective range of 250 Å. A study of the light absorption by the yellow silicomolybdate in synthetic sea water containing 0.070 mg. at. of silicon per liter showed that the maximum absorption occurs in the violet end of the spectrum. Therefore the S-43 filter with average wave length 4300 Å. was used for the remaining measurements.

TIME OF COLOR DEVELOPMENT. The intensity of the yellow coloration has been shown to be somewhat dependent upon the time elapsed after development. Dienert and Wandenbulcke thought that the maximum color developed within 10 minutes, but that fading did not begin for 3 or 4 hours. Swartz (12) investigated this factor and reported that the maximum color developed instantly. The authors found that photometrically the full color development occurs within 3 minutes and does not fade for at least 2 hours.

TEMPERATURE EFFECT. The temperature at which reaction takes place influences the intensity of color formed in certain

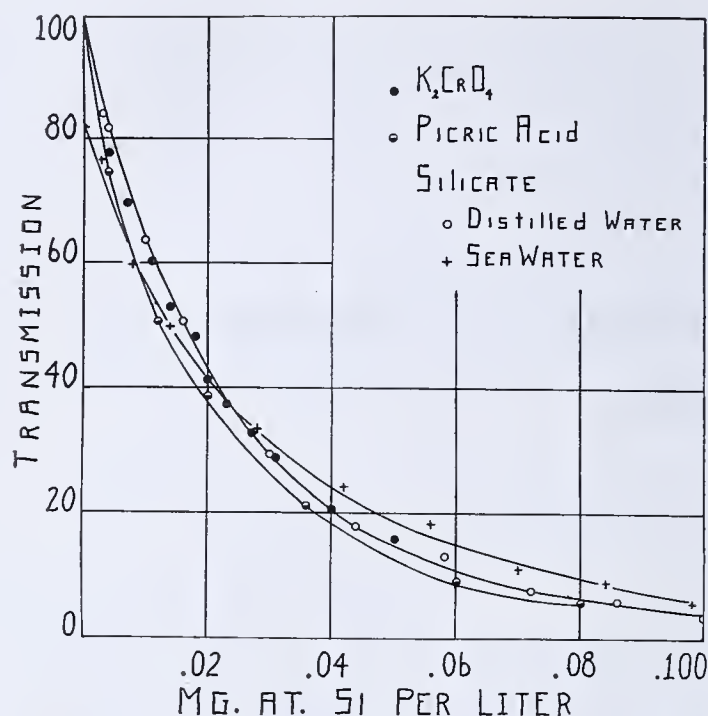


FIGURE 1. PHOTOMETRIC TRANSMISSION CURVES FOR POTASSIUM CHROMATE, PICRIC ACID, AND SODIUM SILICATE

In distilled water and in synthetic sea water, using a 25-cm. cell. Concentrations of potassium chromate and picric acid expressed in terms of silicate equivalencies.

colorimetric methods. Thompson and Houlton (13) found that temperature had no appreciable effect on the development of the silicomolybdate in sea-water solutions; Brujewicz (3), also working with marine waters, asserted that 1 to 2 per cent less color formed with a 10° to 15° C. lowering of temperature, though the authors do not understand how his method of determination possessed such an accuracy. The temperature effect was investigated photometrically by the authors for both distilled water and synthetic sea-water mediums at temperatures of 22° and 6° C. No difference in color intensity could be detected.

COMPARISON OF COLOR INTENSITY WITH WINKLER AND WANDENBULKE REAGENTS. A repetition of the work of Swank and Mellon (11) with fresh waters confirmed their findings that the Winkler reagent with hydrochloric acid yielded 1.09 times as much color for the same amount of silicate as the reagent of Wandenbulke with sulfuric acid. In synthetic sea water the color intensity was essentially the same with either reagent.

HYDROGEN-ION CONCENTRATION AND COLOR INTENSITY. Dienert and Wandenbulke studied the effect of acidity upon the reaction and noted that an excess of acid depressed the formation of the yellow silicomolybdate compound. When Atkins (2) first applied the method to marine waters, a blue coloration developed with the acidity that Dienert and Wandenbulke recommended which was eliminated only when the hydrogen-ion concentration was decreased to a pH of 2. Photometric investigation of the effect of pH demonstrated that the maximum color developed in the synthetic sea water between a pH of 1.5 and 2.3. With increasing acidity, slightly less color was developed.

CALIBRATION CURVES. Silicate in fresh water has been determined photometrically by Strohecker over a considerable range of concentrations with a 3-cm. cell. However, many waters contain less silicate than may be estimated accurately with a cell of this length. For such waters 5- and 25-cm. cells possess more desirable ranges. Photometric calibration curves were prepared for both fresh water and synthetic sea-water mediums in such cells. The data are recorded in Table I and Figure 1. Transmission data were also obtained for picric acid and potassium chromate at these concentrations to permit comparison with the silicate curves. The data have not been included in this paper, but the transmission curves for the 25-cm. cell are shown in Figure 1, where the concentrations of both the picric acid and potassium chromate standards have been plotted in terms of their silicate equivalencies. For the calibration of these permanent standards for the colorimetric silicate determination reference is made

to the work of King and Lucas (6) for picric acid and Swank and Mellon (11) for potassium chromate.

The potassium chromate standards were buffered with sodium borate according to the directions of Swank and Mellon. Comparison of the various curves in Figure 1 showed that the chromate standards agreed more closely with the silicate solutions in distilled water than did the picric acid solutions. Swank and Mellon, after their spectrophotometric investigation, also advised the use of the buffered chromate standards in preference to the picric acid standards. Strohecker, too, observed that the chromate standards agreed more closely with the silicate than picric acid above 10 mg. of silicon dioxide per liter, though below this concentration he found satisfactory agreement.

There are several other reasons for selecting potassium chromate rather than picric acid as the standard: (1) The equilibrium in the buffered solution between the chromate and the dichromate ions ensures a definite color intensity. No special means is taken to regulate the equilibrium between the two tautomeric forms of picric acid. (2) The purification of potassium chromate is more convenient. (3) Since the absorption per gram of potassium chromate is less than for picric acid, a larger weight is necessary which lessens the error involved in weighing. (4) Chromate solutions, if permitted to stand in glass containers, have little effect upon glass containers, while dilute picric acid solutions often become contaminated with large quantities of glass slivers.

BEER'S LAW. Normally the yellow silicomolybdate color of the unknown solution is compared with permanent stand-

TABLE I. TRANSMISSION DATA OF SODIUM SILICATE SOLUTIONS

Silicon Mg. at./l.	Reading I	-Log I/I ₀	Silicon k/mg. at.
Distilled Water Medium, 25-Cm. Cell			
0.000	100.0	0.000	...
0.004	82.0	0.086	0.86
0.010	64.0	0.194	0.77
0.016	51.0	0.292	0.73
0.030	29.5	0.530	0.71
0.044	19.0	0.721	0.66
0.058	13.4	0.873	0.60
0.072	7.7	1.114	0.62
0.086	5.9	1.230	0.57
0.100	3.4	1.469	0.59
0.114	2.1	1.668	0.59
0.128	1.8	1.757	0.55
0.142	1.3	1.886	0.53
Synthetic Sea Water, Cl = 17.32%/100, 25-Cm. Cell			
0.000	82.5	0.000	...
0.003	76.7	0.032	0.43
0.008	60.0	0.138	0.69
0.014	50.0	0.217	0.62
0.028	33.7	0.388	0.55
0.042	24.2	0.531	0.51
0.056	18.5	0.649	0.46
0.070	11.2	0.863	0.49
0.084	8.6	0.983	0.47
0.098	5.7	1.161	0.47
Distilled Water, 5-Cm. Cell			
0.000	80.0
0.007	74.5	0.032	0.91
0.018	66.5	0.070	0.78
0.030	60.0	0.125	0.83
0.056	49.5	0.209	0.75
0.086	41.0	0.290	0.68
0.114	33.0	0.384	0.68
0.142	27.5	0.464	0.65
0.170	21.5	0.570	0.67
0.199	17.8	0.652	0.65
0.227	14.2	0.751	0.66
0.256	12.5	0.807	0.63
0.283	11.5	0.843	0.60
Synthetic Sea Water, Cl = 16.08%/100, 5-Cm. Cell			
0.000	73.0
0.006	68.2	0.029	0.97
0.017	63.2	0.062	0.73
0.028	58.2	0.099	0.71
0.056	52.5	0.143	0.51
0.084	43.7	0.223	0.53
0.113	36.3	0.303	0.54
0.141	31.1	0.370	0.52
0.170	27.3	0.427	0.50
0.197	23.1	0.499	0.51
0.225	20.2	0.558	0.50
0.256	17.0	0.633	0.49
0.281	15.0	0.688	0.49

ards prepared by dilution of a more concentrated standard solution. Obviously Beer's law is assumed to apply not only where the permanent standards are diluted, but also to the silicate solution; or if it does not apply, to deviate identically with both solutions. The applicability of Beer's law may be tested by plotting the negative logarithm of the transmission against the silicate concentration. If the law is valid a straight line is obtained.

In the case of the 25-cm. cell a definite blank transmission was noted when the synthetic sea water was compared with the distilled water reference standard. With the 5-cm. cell, characteristic blanks, I_0 , were obtained with both distilled water and synthetic sea-water mediums, since air was the reference standard. To bring these curves to a more comparable basis all the original transmissions, I , were divided by the blank transmissions, I_0 . It is the negative logarithms of these recalculated transmissions which have been plotted in Figure 2. Recalculation did not change the slope of the curve, but merely the intercept.

On investigation, Beer's law was found to apply only approximately, as the curves were not perfectly straight. This was particularly true for concentrations greater than 0.20 mg. at. of silicon per liter. For concentrations less than this, the curves deviated but slightly from a straight line. The applicability of Beer's law may also be determined from an examination of the specific extinction coefficient per milligram atom listed in column four of Table I. The specific extinction coefficients were calculated by dividing the negative logarithm of the transmission by the cell length and the silicate concentration. Beer's law applies if the specific extinction coefficient remains constant throughout, which was not the case for silicate. The values for the distilled water medium show general agreement with those of Strohecker when they are converted to a common basis.

SALT EFFECT. It was also noted that for the same silicate concentration less silicomolybdate color developed in a salt-water medium than in fresh water. The effect of varying chlorinities, 7.00, 11.8, 16.08, and 19.00‰, was determined using the 5-cm. cell. Though increasing chlorinity slightly diminished the intensity of the silicomolybdate color, the effect was too small to be significant. In view of this fact only the data for a single chlorinity have been given with each cell—17.32‰ for the 25-cm. cell and 16.08‰ for the 5-cm. cell.

A measure of the salt effect may be obtained from the ratio of the slopes of the curves demonstrating the validity of Beer's law in Figure 2. The fresh-water curve for the 5-cm. cell had a slope of 3.49 and the salt-water curve 3.01, which yielded a ratio of 1.16. Approximately the same value was obtained from the curves with the 25-cm. cell. This value is considerably lower than that found by Brujewicz and Blinov by another method. They reported a correction factor of 1.66 for the salt error, which is a value larger than might be anticipated.

All previous colorimetric silicate values for ocean waters obtained by colorimetric methods are then too low. To be corrected they should be multiplied by the factor 1.16. With low silicate values the correction would be insignificant. However, in the future when permanent standards are to be used for the determination of silicate in marine waters it is recommended that the standard be adjusted to compensate the salt effect.

Summary

From a photometric study of the determination of silicate in marine waters, it was concluded that (1) the maximum

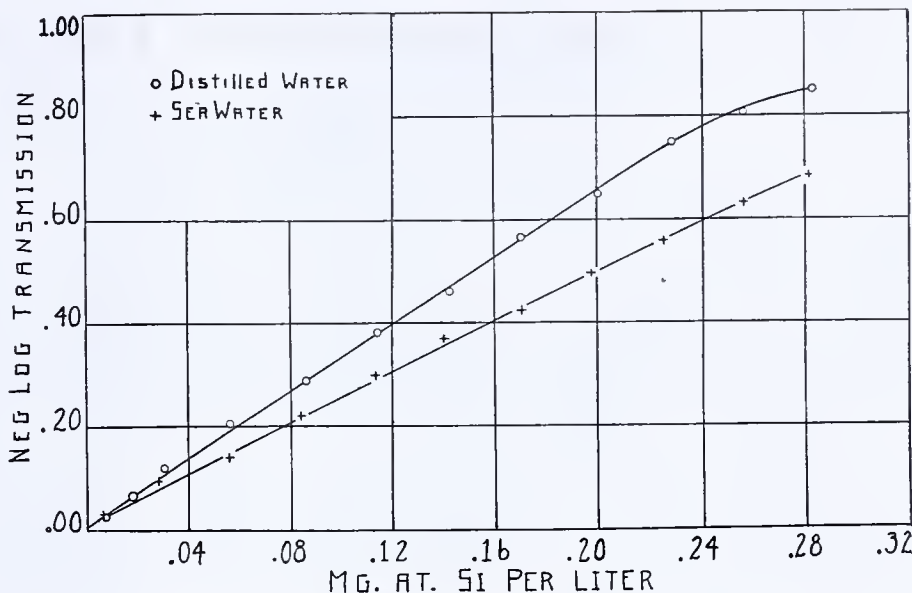


FIGURE 2. NEGATIVE LOGARITHM OF TRANSMISSION PLOTTED AGAINST SILICATE CONCENTRATION (Using a 5-cm. cell)

silicomolybdate color develops within 3 minutes and is constant for at least 2 hours; (2) a variation in temperature of 10° to 15° C. at the time of development does not influence the color; (3) the maximum color is developed between a pH of 1.5 and 2.3; (4) in marine waters the reagents of Winkler and Wandenbulcke both yield the same color intensity.

The maximum absorption occurs with a filter having an average wave length of 4300 Å. Calibration data are given for 5- and 25-cm. cells. Beer's law was found to apply only approximately over the range of concentrations studied. Less silicomolybdate color develops in a saline medium than in a fresh-water medium. To correct previous determinations which are somewhat in error, a factor of 1.16 should be used. Potassium chromate solutions are recommended rather than picric acid if permanent standards are to be used.

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RECEIVED July 13, 1936.

CORRECTION. In the article entitled, "A System for the Qualitative Analysis of the Alkaline Earth and Alkali Groups" [*IND. ENG. CHEM., Anal. Ed.*, 8, 346 (1936)], the reagent employed to detect magnesium was wrongly called *p*-hydroxybenzene-azoresorcinol. The substance used was *p*-nitrobenzene-azoresorcinol, as is stated in the section on procedure.

CHARLES H. GREENE

Conductometric Determination of Enzyme Activity

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THE possibility of utilizing changes in electrical conductivity for measuring enzyme activity has been shown by the work of Sjoquist (11), Oker-Blom (10), Henri and des Bancelles (6), and Bayliss (1, 2). More recently, Northrop (7, 8, 9) in the course of his studies has utilized the method for (1) estimating pepsin, (2) determining the ionization of egg albumin-hydrochloric acid with a view to elucidating the dependence of hydrolysis on substrate ionization, and (3) studying the kinetics of tryptic digestion in relation to its mechanism. Euler (5) has employed the method for studying the hydrolysis of glycylglycine. Bayliss (3) has suggested the possibility of employing electrical conductivity for investigating the action of urease, lipase, and the glucosidase, myrosin, but does not report any investigation relating to these systems.

For purposes of conductometric estimation, enzyme reactions can be classed as (1) those that release strong electrolytes, (2) those that release feebly ionizing ampholytes, and (3) those that give rise to what are conventionally known as nonelectrolytes, like sugars. Urea-urease, sinigrin-myrosin, and methylglyoxal-glyoxalase are among those comprising the first group, while the protein-proteolytic systems, resulting in the production of amino acids, belong to the second group.

Changes in electrical conductivity accompanying the enzyme hydrolysis of urea, arginine, and peptone have been measured. The changes are shown to be strictly proportional to the release of ammonium carbonate in the first two systems and of amino groups in the third. The conductometric method finds application in the determination of enzyme and substrate concentrations in various physiological fluids.

The third group is represented by carbohydrases and the majority of glucosidases which, acting on their respective substrates, release sugars. The reactions belonging to the first group are obviously best suited for conductometric studies. The second group reactions offer certain difficulties and impose certain limitations but can nevertheless be followed by employing a sensitive device. The third

group reactions which, for the present, lie beyond the scope of these studies, could be brought within their scope by taking advantage of the fact that, in presence of borates, arsenates, and molybdates, polyhydric alcohols like sugars exhibit an increase in their electrical conductivity.

The strongest objection put forward against the employment of this method is that the reactions cannot be studied in buffered systems. For determining enzymic activities, we are concerned essentially with the course of action in the initial stages when the disturbing factors, due not only to the changes of reaction but also to the accumulation of products of hydrolysis, are at a minimum. During this period the conductivity method is perhaps the only one which could be applied with any advantage, since it is capable of giving a large number of values for the early stages of the reaction. Further, there are reactions where very little change occurs

in the pH of the medium; thus, Northrop (9) found that at pH 6.2 to 6.4 the hydrolysis of gelatin by trypsin is not accompanied by any alteration in pH. The presence of electrolytes in small concentrations as impurities in the reacting mixture does not interfere with the measurements, since appropriate conductivity cells can be chosen to give the desired accuracy.

In common with other physical methods, conductivity measurements have the advantage of being carried out without disturbing the course of action and can be made applicable to very small quantities of substrates.

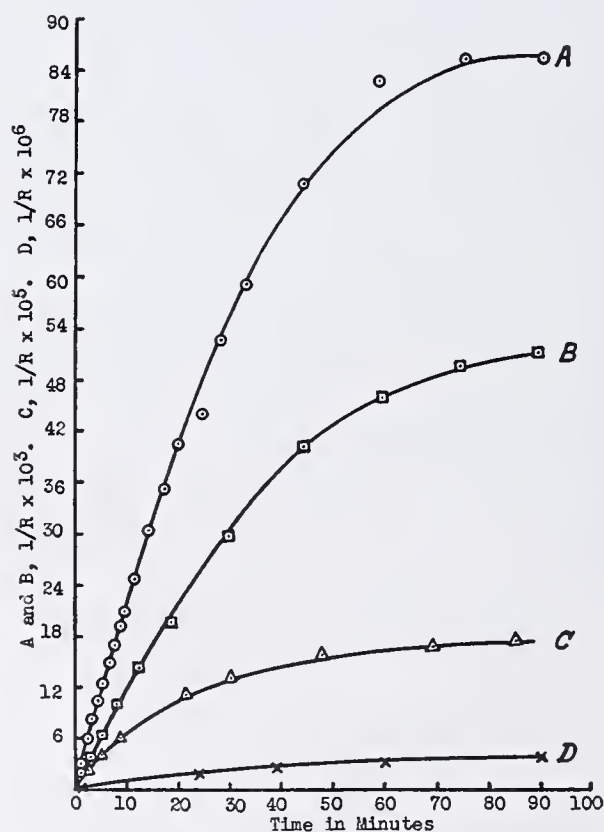


FIGURE 1. CONDUCTOMETRIC METHOD

- A. Urea-urease
- B. Arginine-argininase-urease
- C. Peptone-trypsin-kinase
- D. Salicin-emulsin

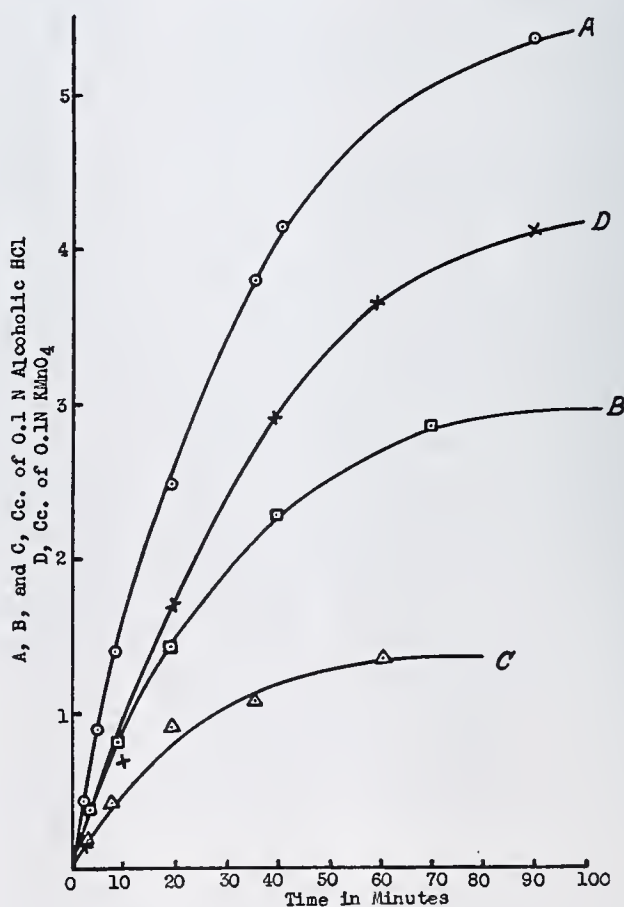


FIGURE 2. CHEMICAL METHOD

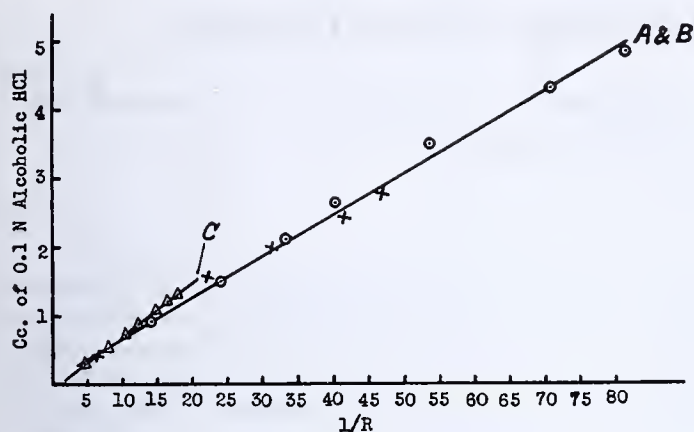


FIGURE 3. CORRELATION GRAPHS

Experimental

The present communication deals with a conductometric study of urea-urease, arginine-arginase-urease, peptone-trypsin-kinase, and salicin-emulsin.

For the measurement of conductivity the usual Kohlrausch bridge method was employed. A calibrated Kohlrausch slide wire, a 4-dial resistance box, and an Arrhenius-Ostwald cell formed the components of the circuit. A 5-cc. aliquot of the substrate solution was all that was necessary for the work. Platinized electrodes were employed and the cell was immersed in a water thermostat electrically maintained at $30.0^\circ \pm 0.1^\circ \text{C}$. The audio oscillator (General Radio Co.) giving an alternating current with a frequency of 1000 was employed as the source of high-frequency current and a telephone receiver was used for detecting the null point. The capacitance of the conducting cell was balanced by means of an air-condenser which was connected in parallel with the resistance box. Readings were taken at short intervals at the commencement of the reaction and later at longer intervals. Experiments with larger quantities were simultaneously carried out in a separate reaction vessel, the same relative enzyme-substrate concentration being employed. Aliquots of the reaction mixture, withdrawn from the reaction vessel at definite intervals, were analyzed and the course of the reaction was thus followed by an entirely independent chemical method.

UREA-UREASE. A 1 per cent solution of urea (Kahlbaum) and an aqueous solution of soya urease precipitated by acetone were employed. The release of the ammonium carbonate was followed by the method developed by Sastri in 1935 (4), which consists in titrating aliquots of the reaction mixture in the presence of acetone against standard alcoholic hydrochloric acid (0.1 N).

ARGININE-ARGINASE-UREASE. Arginine carbonate was prepared from *D*-arginine, a solution of 0.5 per cent being saturated with carbon dioxide. The excess of carbon dioxide was removed by bubbling electrolytic hydrogen through the solution. The solution of arginine carbonate thus obtained showed a steady value for conductivity. An aqueous extract of the acetone-precipitated liver extract of a ram was employed as the source of arginase. By using an excess of urease an almost instantaneous hydrolysis of the urea, progressively released during the decomposition of arginine, was secured so that the reaction mixture at any one time contained only ornithine and ammonium carbonate. The quantity of ammonium carbonate in the reaction mixture was estimated at different intervals of time by the titrimetric method referred to above.

PEPTONE-TRYPSIN-KINASE. A 1 per cent aqueous solution of Witte's peptone (B. D. H.) and 1 per cent solution of Pfanstiehl's preparation of trypsin-kinase were employed. The proportion of the substrate to enzyme was 10 to 1. The amino groups released during the hydrolysis were estimated by Linderström Lang's titrimetric method.

SALICIN-EMULSIN. A 1 per cent solution of salicin and an aqueous extract of emulsin (B. D. H.) were used. The sugar released was estimated by Bertrand's method.

Discussion

The measurements, both conductometric and chemical, were carried out for at least two enzyme concentrations. The results of one set of experiments are graphically represented in Figure 1 (conductometric) and Figure 2 (chemical).

The general shape of the two corresponding sets of curves indicates that the kinetics of these enzyme reactions can be followed conductometrically. The close relation between the physical and chemical methods is clearly brought out by the correlation graphs (Figure 3) prepared according to the method previously described (12). In the two systems urea-urease and arginine-arginase-urease, the change in conductivity is essentially due to the release of ammonium carbonate and this is strikingly brought out in the graphs. The correlation graphs (Figure 3) for urea-urease and arginine-arginase-urease are practically identical. The change in electrical conductivity per millimole release of amino acid can be calculated in the peptone-trypsin system also; there is a correlation between the change in conductivity and the release of amino groups. For the study of the salicin-emulsin system, however, the chemical method is by far the more accurate, since the changes in conductivity accompanying the system, although easily measurable and reproducible, are very slight in magnitude. The possibility of increasing the conductivity of the sugar released by the addition of borates is being investigated. At the moment the conductometric method, so far as sugar-releasing systems are concerned, offers no special advantage over the chemical method.

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RECEIVED June 20, 1936.

Correction

In an article entitled "The Sampling and Analysis of Eggs" [IND. ENG. CHEM., Anal. Ed., **8**, 377 (1936)] the authors submitted a glycerol and a salt method with the statement that "here no A. O. A. C. method applies," and it has been called to our attention that this would imply that no A. O. A. C. method is available for these analyses.

This is not the case. The A. O. A. C. method for chlorine on page 249 of the third edition of the "Methods of Analysis" of the association may be revised for the determination of salt in quantities such as are present in salt yolk. However, the time required for a series of determinations by this method is over 12 hours as against 10 minutes for the method we published. Similarly a method for glycerol published [*J. Official Agr. Chem.*, **15**, 334 (1932)] and tentatively adopted [*Ibid.*, **16**, 74 (1933)] requires 6 hours for six determinations as contrasted with 1.5 hours for a similar number of determinations by our method.

Since our purpose, as mentioned in the third paragraph of our paper, is to give rapid methods which yield reproducible results, we omitted reference to the above A. O. A. C. methods which are not suitable for plant control and trust that no ambiguity will have arisen because of such an omission.

W. S. GUTHMANN
W. L. TERRE

Free Sulfur in Petroleum Distillates

Effect of Peroxides upon the Copper-Strip Method. Quantitative Method for the Determination of Free Sulfur

S. COMAY, 356 West 34th St., New York, N. Y.

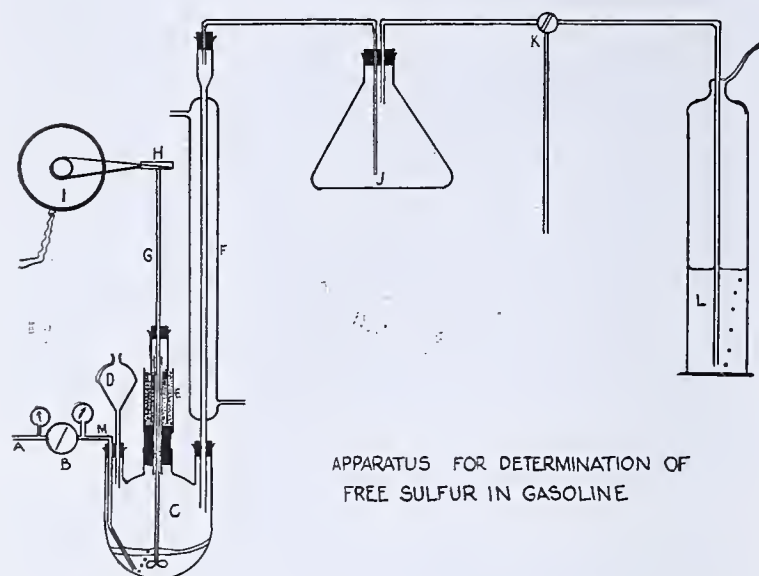


FIGURE 1. APPARATUS FOR DETERMINATION OF FREE SULFUR IN GASOLINE

- | | |
|----------------------------|-----------------------------------|
| A. Inert gas supply | I. Variable-speed motor |
| B. Reducing valve | J. Trap (100-cc. Erlenmeyer) |
| C. 3-Neck liter flask | K. Three-way stopcock |
| D. Dropping funnel, 50 cc. | L. Gas-washing bottle for absorb- |
| E. Mercury seal | ing hydrogen sulfide filled |
| F. Condenser | with ammoniacal cadmium |
| G. Stirrer | chloride solution |
| H. Pulley | M. Gas inlet tube |

FREE or elementary sulfur is present in nearly all cracked and straight-run gasolines, but its presence in crude oils has not been established generally.

A Pennsylvania crude oil, which had the usual sulfur content, was analyzed and found to contain no hydrogen sulfide, free sulfur, or mercaptans. When about 50 per cent of the crude oil had been taken over by fire-distillation, the overhead product contained hydrogen sulfide, free sulfur, and a mercaptan or mercaptans in small amounts. Birch and Norris (4) report that when a distillate from maidan-i-naftun was heated to 120° C., free sulfur appeared in the distillate. This finding, if true, is an extraordinary case and an exception to the rule, unless the free sulfur was formed by oxidation of hydrogen sulfide in the receiver. If free sulfur was present originally in the crude oil or, as these authors state, was a product of decomposition in the liquid phase in the still, it would not distill at such a low temperature and concentration. A gasoline to which 0.10 per cent of sulfur had been added gave no free sulfur in the distillate when the vapor temperature had reached 150° C. It has been found, however, that sulfur does appear at a vapor temperature of 200° if the distillation is conducted rapidly. The partial pressure of sulfur is relatively high at this temperature and the rapidity of the distillation does not permit the sulfur to react completely with the hydrocarbons. These distillations were conducted through a Hempel column.

Hoffert and Claxton (11) claim that free sulfur in motor benzene distills over when open steam is used at 100° C. Many steam distillations made by this author contest this assertion strongly. A gasoline to which 100 mg. of free sulfur per 100 cc. were added gave no elementary sulfur in the overhead product when it was steam-distilled at 150° to 160° C.

The occurrence of free sulfur in the products of distillation of a sulfur-bearing charging stock is easily explained by the results obtained by Faragher, Morrell, and Comay (9) in their investigation of the thermal decomposition of organic

sulfur compounds. Free sulfur may also appear as an oxidation product of hydrogen sulfide either by air-oxidation or by the action of sulfur dioxide. The presence of free sulfur in gasoline finished by the so-called sweetening process is too well known in the petroleum industry to require elaboration. Free sulfur in any motor spirit presents a serious problem; it is very corrosive to many parts of the fuel system, as has been shown by Hoffert and Claxton (11) in their exhaustive investigation of the corrosive effect of elementary sulfur upon copper.

Various methods have been proposed for the quantitative determination of free sulfur. The Ormandy and Craven method (14), modified by the Institution of Petroleum Technologists and adopted as a British Standard Method (5), yields accurate and reproducible results and is perhaps the best so far proposed, although slow and tedious. The method is based on the conversion of free sulfur to mercuric sulfide by shaking with mercury. Recently Garner (10) proposed as a quantitative method for the determination of free sulfur refluxing the gasoline samples in the presence of copper bronze and then oxidizing the copper sulfide to sulfate by bromine. The sulfate is determined as barium sulfate in the usual manner.

The American petroleum industry has no generally used method for the quantitative determination of free sulfur but uses the qualitative method of the American Society for Testing Materials (1), known as the copper-strip method. That the copper-strip method is not reliable has been demonstrated in several cases by Hoffert and Claxton (11). No corrosive effect upon the copper was observed with some samples of benzene even in the presence of over 5 mg. of free sulfur per 100 cc. These investigators attempt to explain the failure of the free sulfur to corrode under the conditions of the test by the presence of impurities, such as sulfur dioxide, dialkyl esters of sulfuric acid, sulfonic acids, etc., that act as inhibitors. That none of these compounds has any inhibitory effect has been proved in actual tests. An untreated cracked gasoline that gave a positive corrosion test by the copper-strip method failed to do so after several weeks of standing. A consideration of this phenomenon led to the conclusion that oxidation was the principal change that had occurred in the sample and that its products were involved in the failure of the test.

It was later found that no indication of corrosion was shown on the copper after several hours at 100° by some oxidized gasolines to which 100 mg. of free sulfur per 100 cc. of gasoline were added. But when the gasolines were treated with sulfur dioxide for 5 minutes, washed with caustic soda, and tested with a copper strip, heavy corrosion and scaling occurred after a few minutes at room temperature. Brooks (6) to the author's knowledge was first to employ sulfur dioxide in detecting the presence of peroxides in gasoline. The same results were obtained when the peroxides were reduced with a water-alcohol solution of ferrous sulfate. A series of experiments was made, the more striking results of which are given in Table I.

After this work was almost completed, a paper by Kiemstedt (12) reported that peroxides are inhibitory agents in the corrosive action of free sulfur on copper. Although peroxides were found to be the inhibiting agents that affect the corrosive action of free sulfur upon copper, the mechanism

of this phenomenon is not easily understood, especially in the light of the results obtained by Hoffert and Claxton (11) concerning the composition of the black deposit formed. They found that it consists almost entirely of cuprous and cupric sulfides. They report that in the absence of impurities that act as inhibiting agents the deposit from pure benzene and sulfur approximates cupric sulfide in composition, while those formed by the action of crude benzenes on copper contain a much larger proportion of the cuprous compound. Hoffert and Claxton say that this difference is "probably explained by the later discovery that the presence of other impurities in the benzene tended to inhibit the action of free sulfur on copper." It is rather beyond possibility that peroxides, which are the true inhibitory impurities, should act as reducing agents in the reaction between copper and sulfur.

It must be emphasized that the accumulations of peroxides will cause the A. S. T. M. method, known as the copper-strip test, to fail to show the presence of free sulfur. On the other hand, the mercury test alone cannot be used as a qualitative test for free sulfur, since it was shown by Kingzett (13) and Antropoff (2) that peroxides give a black deposit with mercury.

It follows, therefore, that in order to show qualitatively the presence of free sulfur, the peroxides in the sample of gasoline must be reduced. The reduction is readily accomplished either by sulfur dioxide or an aqueous solution of ferrous sulfate to which alcohol is added. The sample may then be tested either with mercury or by the copper strip.

It follows that the method proposed by Garner for the quantitative determination of free sulfur will fail in case of aged or oxidized gasolines, and if this method is used the gasoline must first be reduced to eliminate the peroxides.

TABLE I. INHIBITORY EFFECT OF PEROXIDES UPON ACTION OF SULFUR ON COPPER

No. of Expt.	Solution Sulfur Peroxide		Effect on Copper Strip	Time
	Mg.	Mg./100 cc.		
1	100	None	Discoloration	Instantaneous
2	50	None	Discoloration	Almost instantaneous
3	50	50	No discoloration at 212° F.	After 2 hours
4a	75	25	No discoloration at 212° F.	After 15 minutes
4b	75	25	Slight spotty discoloration at 212° F.	After 2 hours
5a	87.5	12.5	No discoloration at 212° F.	After 5 minutes
5b	87.5	12.5	Discoloration at 212° F.	After 15 minutes
6	95	5	Discoloration	Instantaneous scaling after 5 minutes
7	90	10	Discoloration	Instantaneous

For reducing the peroxides, sulfur dioxide or a water-alcohol solution of ferrous sulfate was mentioned. The question arose of using nascent hydrogen—subjecting the oxidized gasoline to the action of zinc and hydrochloric acid. The answer was soon obtained by an actual test with the oxidized sample of gasoline to which 100 mg. of free sulfur per 100 cc. were added and which failed to give the corrosive test in the copper-strip test. Not only were the peroxides reduced but the free sulfur also was reduced to hydrogen sulfide. Therefore, this ready reduction of free sulfur by nascent hydrogen can be easily utilized for a quantitative method of free sulfur in gasoline or any other motor fuel.

Quantitative Method for Determination of Free Sulfur

The principle underlying the newly proposed method for the quantitative determination of free sulfur is in reality based upon the discovery by Cloez (?) in 1858 that hydrochloric acid and zinc, aluminum, or iron convert free sulfur suspended in water into hydrogen sulfide. Cossa (8) obtained the same conversion of free sulfur, suspended in water, into hydrogen sulfide by electrolysis of the water.

It has been found that the action of nascent hydrogen in converting free sulfur dissolved in gasoline is very rapid and complete. Therefore, it was not difficult to devise an apparatus in which the hydrogen sulfide could be formed and driven out readily from the gasoline into an ammoniacal solution of cadmium chloride. Titration with iodine solution by the usual analytical procedure was used to determine the hydrosulfide.

When zinc dust and hydrochloric acid were used, although all the sulfur present was converted into hydrogen sulfide and all the sulfide was driven out from the apparatus, low results were obtained in most of the tests made, especially when a large amount of zinc dust was used. This was found to be due to zinc sulfide suspended between the gasoline and acid layers. For this reason, iron powder, reduced by hydrogen, was used. The results are given in Table II.

TABLE II. QUANTITY OF SULFUR DETERMINED BY REDUCTION

Sulfur Used	Sulfur Found	Sulfur Used	Sulfur Found
Mg.	Mg.	Mg.	Mg.
10	9.92	3	3.01
10	9.83	3	3.04
10	9.92	3	3.01
5	4.98	2	1.98
5	4.96	2	2.03
5	4.95		

An experiment with a solution of 2 per cent di-isoamyl disulfide gave no hydrogen sulfide, but mercaptans were formed as a result of the reduction.

Description of Apparatus

The apparatus consists of a cylinder supplying hydrogen or nitrogen through A, connected by rubber tubing to a glass inlet tube, M, that nearly reaches the bottom of the flask, C. The stopper holds also dropping funnel D, leading almost to the bottom of three-neck round-bottomed flask C. Through the central neck of the flask the stirrer, G, supplied with mercury seal E is inserted; the remaining side neck of C is used for condenser F, connected by glass tubing to trap J (serving for trapping any gasoline that may be swept out from C), which is connected by glass and rubber tubing to three-way stopcock K and then to gas-washing bottle L.

Procedure

The synthetic solutions of free sulfur were made in a naphtha that had an initial boiling point of about 135° C. Five grams of iron reduced by hydrogen (containing 0.03 per cent of sulfur) were placed in three-neck flask C and the sample of naphtha was added. The apparatus was then closed, the stirrer, G, started, and hydrochloric acid (1 to 4) added in several portions through the dropping funnel, D. Usually, 40 cc. of the hydrochloric acid are more than enough. As soon as the acid covers the reduced iron, gas is evolved. The addition of the acid is stopped until the evolution of the gas ceases, then acid is added and the procedure repeated. After 10 or 15 cc. of acid have been added, the precipitate of cadmium sulfide in the gas-washing bottle, L, appears. After all the acid has been added the iron will have disappeared. Inert gas from A is allowed to bubble through the liquids in flask C, which are heated to about 80° C. In order to determine whether or not the hydrogen sulfide has been driven out, gas is released through the cock, K, and is tested with cadmium chloride solution.

The complete test requires less than 20 minutes. After the test is completed, the gasoline in C must be tested for free sulfur by shaking with mercury and for hydrogen sulfide with lead acetate paper. Obviously, running blank tests for the sulfur content in the reduced iron powder is a precaution not to be avoided. Cleaner's naphtha free from elementary sulfur may be readily used in the above procedure for the determination of sulfur in the reduced iron. Since the percentages of free sulfur in petroleum distillates are small, it would be advisable to use the purest obtainable iron powder, reduced by hydrogen.

In order to utilize this method for determining elementary sulfur present in gasoline, the following procedure is suggested:

Two hundred cubic centimeters of the gasoline to be tested are vacuum-distilled till about 50 per cent comes over. The sulfur determination is then made on the residue and the result obtained is calculated as milligrams of sulfur per 100 cc. of gasoline.

Birch and Norris (3) stated that a copper-corroding substance is obtained when a petroleum distillate containing a mercaptan is treated with sulfuric acid. They found that this substance, dialkyltrisulfide, on reduction with zinc and hydrochloric acid, yields a mercaptan and hydrogen sulfide. Therefore, in order to analyze an acid-treated distillate for free sulfur, the quantity of hydrogen sulfide which will be formed by reduction of such substances must be deducted from the total amount of hydrogen sulfide. This can readily be accomplished by treating a sample of the distillate to be analyzed for free sulfur with mercury for the purpose of removing the free sulfur. The sample thus treated is then analyzed by the above described method for the corrosive trisulfide, and the amount of hydrogen sulfide obtained is then subtracted from the total hydrogen sulfide.

All the experimental data, with the exception of the results contained in Tables I and II, were obtained in the laboratories of the Houdry Process Corporation at Paulsboro, N. J. The writer expresses his appreciation for the permission to publish these results, and, especially, feels indebted to W. F. Faragher for his suggestion that peroxides must be the inhibitors which affect the corrosive action of sulfur on copper.

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Metal Extractor for Laboratory Use

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IN THE course of chemical and biochemical studies and analyses, it is frequently necessary to extract various quantities of such materials as wheat germ, casein, or protein meals. The usual glass apparatus found in laboratories is rather difficult to set up so as to form a continuous extractor. Soxhlet and other extractors are not ordinarily of sufficient size to permit use of large samples. McCay (2) and Bryant (1) have described apparatus which work well for relatively large amounts of material (20 to 50 pounds).

As no simple and inexpensive apparatus for the continuous extraction of from 1 to 5 pounds of material was found listed in various scientific catalogs, the extractor illustrated in Figure 1 was designed for use in this laboratory. Two are

now in use and have proved to be efficient and to require very little attention.

A is a 20-quart cream-setting can, 9 inches in diameter and 20 inches high, supplied with a cover which fits closely over the top and 2 inches down the side. The condenser, B, consists of a 15-foot spiral of soft-copper tubing 0.25 inch in outside diameter and is soldered inside this cover, approximately even with the bottom edge of the lid. In bending this type of tubing, it is necessary to fill it with some material which will prevent its collapsing; in this instance, the tubing may first be filled with fine dry sand and the ends tightly stopped. After the bending is completed, the sand is easily removed by lightly tapping the tubing and revolving the coil at the same time.

The container for the material, C, is made by removing the bottom of a 5-pound ether can. A copper siphon tube, D, is soldered through the cap of the can and bent so that the top of the siphon loop is about two-thirds up the side of the container. The end of the siphon extends about 2 inches below the side of the can. The extractor is supported by an ordinary iron laboratory tripod, the legs of which have been cut to a length of 7 inches. The tripod is kept in place by three U-strips of tin soldered to the can.

A wire gauze is placed in the bottom of container C and over this is laid a layer of cotton; C is then filled with the material to be extracted and placed inside the large can, A. About one and one-half times as much solvent is added as is necessary for the operation of the siphon. After setting the lid in place and starting a good flow of water through the coil, the can is set on a three-heat, 600-watt electric heater. When using alcohol or acetone the heater is turned on high, but with ether it is advisable to use medium or low heat.

The cost of materials for constructing this apparatus, not including the heater, is less than three dollars.

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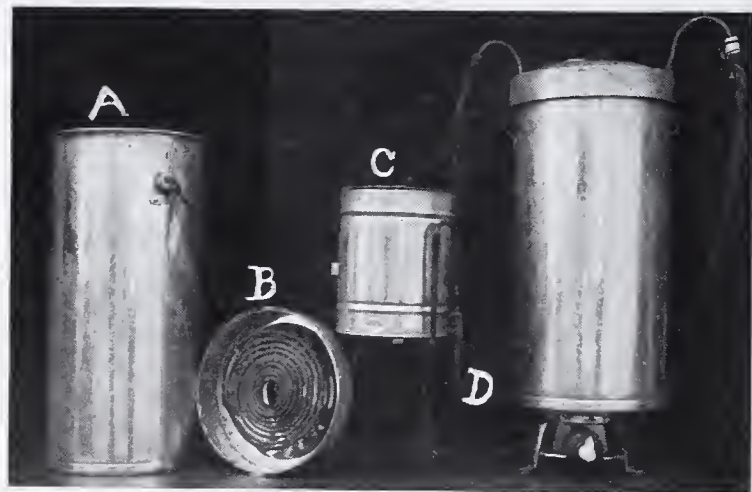


FIGURE 1. EXTRACTION APPARATUS

- A. Cream-setting can
- B. Cover with copper coil
- C. Inside container for material
- D. Siphon tube

The apparatus assembled for use is shown on the right.

Solutions for Colorimetric Standards

VII. Aqueous Solutions of Salts of Elements 23 to 29

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AN INSPECTION of the Bohr form of the periodic table of the chemical elements reveals the interesting fact that the elements forming colored ions in aqueous solution include those assigned to the so-called transition group, together with a few others situated adjacent to or near them. Thus we find no color until element 22 (Ti) is reached. It continues then through the successive elements, 23 to 29 (V, Cr, Mn, Fe, Co, Ni, Cu), disappearing sharply with 30 (Zn).

Aqueous solutions of certain salts of part of these elements have been used for various colorimetric purposes in a number of different ways. Their use in colorimetric analysis has been reviewed before (1, 4, 5, 6). Most of the applications have been in the preparation of permanent standards for use in determining substances whose properties are such as to prohibit their own use for comparison solutions. Thus the 1933 edition of the American Public Health Association's "Standard Methods of Water Analysis" specifies such inorganic standards for the determination of color, ammonia, chlorine, iron, and silica.

In determining the specifications for such a series of standards, the general practice has been to match a known amount of the constituent to be determined with a solution containing one or more of the substances forming colored ions. The match has usually been made on the basis of visual comparison of the two systems. It frequently happens that solutions appearing to be matched with the eye yield quite different

spectral transmission curves. Then, if the two systems are observed under a source of illumination having a spectral energy distribution distinctly different from that of the source used for the original matching, the systems may not appear matched.

In view of the present usage of such systems for colorimetric standards and of the possibility of applying them to some of the many new colorimetric methods, it seemed worth while to make a more exhaustive study of the characteristics of various systems showing promise of possible usefulness in this direction. The present work was limited to elements 23 to 29, together with cerium, and was confined to compounds that seemed most likely to be of value.

Many previous studies have been made on the absorption spectrum of solutions of these compounds. In general, the objective of the work was different, and usually the methods of measurement employed were not capable of giving the quality of results now obtainable with photoelectric instruments.

Experimental Work

MATERIALS. Wherever it was feasible, the salts to be used were recrystallized at least twice from conductivity water, and the latter was used to make all solutions. Concentrations were determined by standard analytical methods. The best analytical practice was followed in preparing solutions of potassium permanganate and ceric sulfate, the latter being made from a double

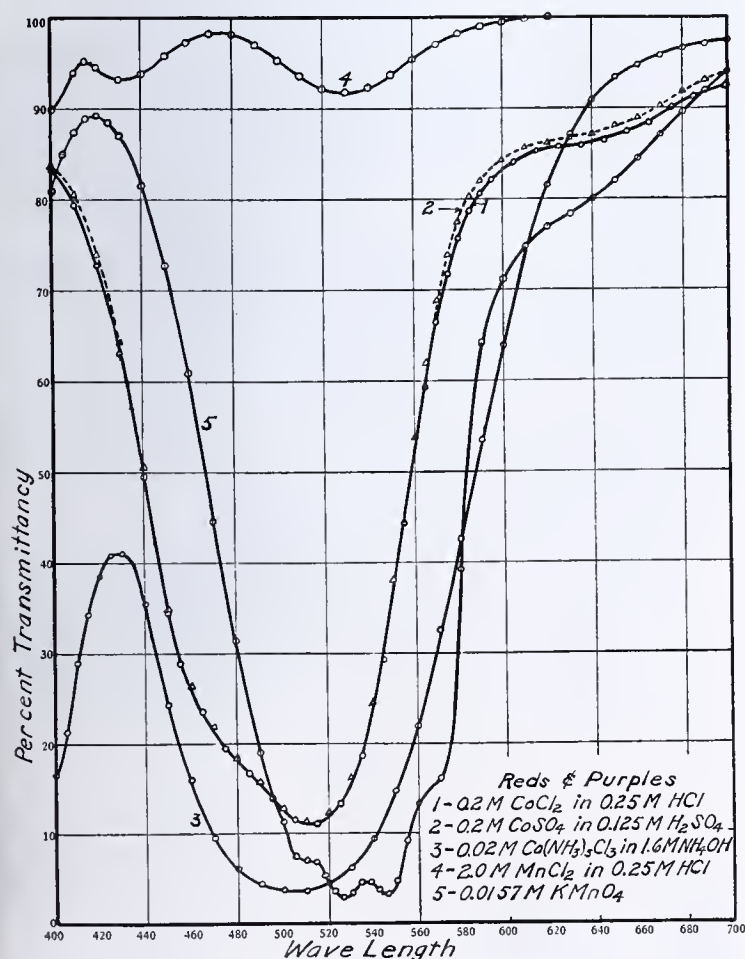


FIGURE 1. SPECTRAL TRANSMISSION CURVES FOR RED AND PURPLE SOLUTIONS CONTAINING SALTS OF COBALT OR MANGANESE

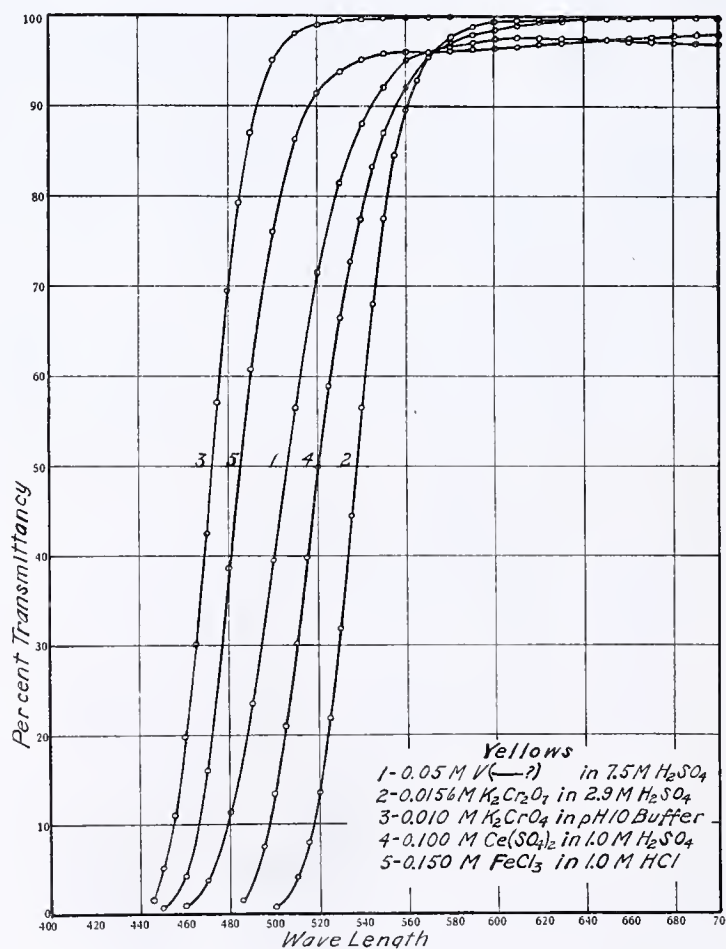


FIGURE 2. SPECTRAL TRANSMISSION CURVES FOR YELLOW SOLUTIONS CONTAINING SALTS OF VANADIUM, CHROMIUM, CERIUM, OR IRON

(The formula for the vanadium compound is uncertain.)

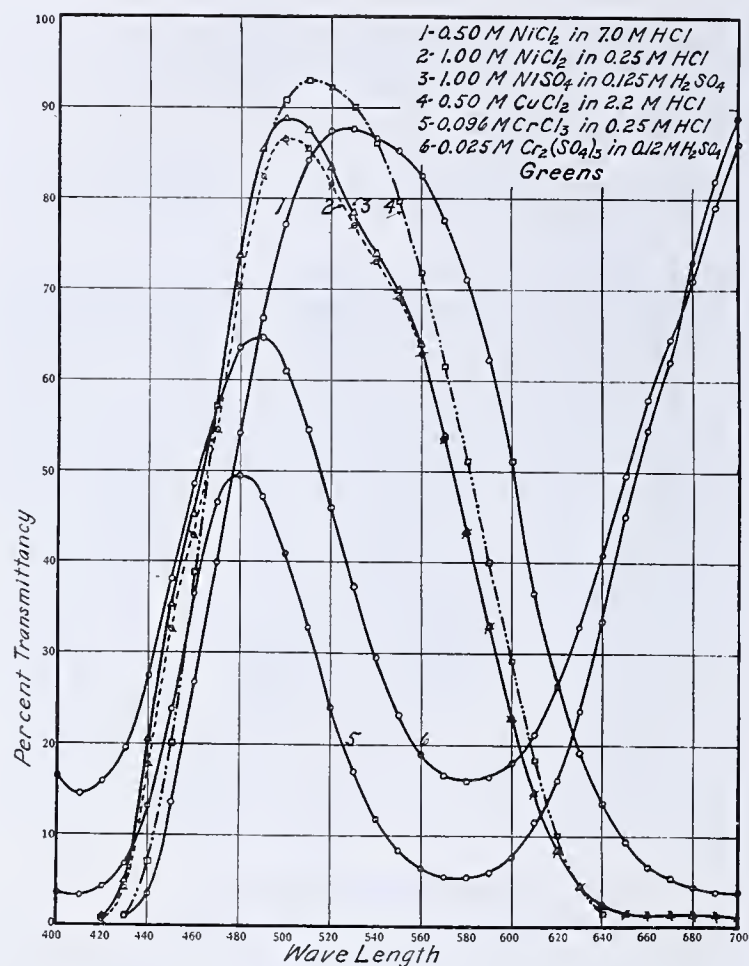


FIGURE 3. SPECTRAL TRANSMISSION CURVES FOR GREEN SOLUTIONS CONTAINING SALTS OF NICKEL, COPPER, OR CHROMIUM

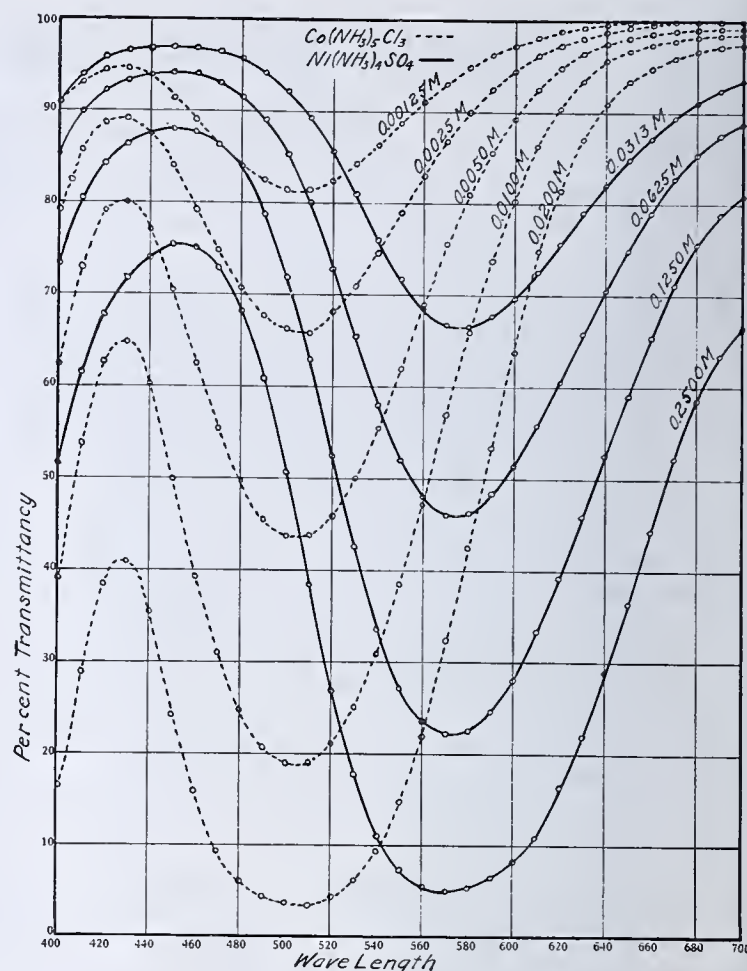


FIGURE 5. SPECTRAL TRANSMISSION CURVES FOR DIFFERENT CONCENTRATIONS OF TETRAMMINO NICKEL SULFATE AND CHLOROPENTAMMINO COBALT CHLORIDE



FIGURE 4. SPECTRAL TRANSMISSION CURVES FOR BLUE SOLUTIONS CONTAINING SALTS OF COPPER, COBALT, NICKEL, OR VANADIUM

ammonium sulfate. A c. p. grade of vanadium pentoxide, free of iron, was dissolved in concentrated sulfuric acid and then diluted in making the yellow solutions. The blue solutions of vanadyl sulfate were made by suspending vanadium pentoxide in hydrochloric acid and bubbling sulfur dioxide or hydrogen sulfide through the solution to accomplish the reduction. The solution was then filtered, analyzed, and diluted. Ferric chloride was made by passing chlorine over hot iron wire and subliming the product.

APPARATUS. The photoelectric spectrophotometer, built by the General Electric Company, has been described by Hardy (2). The method of use, together with advantages of the instrument, was outlined in a previous paper by the authors (3).

DATA. Since spectral transmission curves reveal the colorimetric characteristics of a system more quickly than tabular data, the graphical method has been used here, plotting per cent transmittancy as ordinates and wave length as abscissas. All data were calculated to a basis of 10.0-mm. cell thickness.

Figures 1 to 5 illustrate the results obtained. In Figures 1 to 4 the curves are grouped according to the following hues: reds and purples, yellows, greens, and blues. Each curve is one of a series for different concentrations at a given acidity, or the same concentration at different acidities. Figure 5 shows a limited selection of curves from two such series.

Discussion

The curves as such require little comment. The systems selected for measurement and the range of acidities covered in the solutions seemed most likely to include those of value. Thus, interesting solutions, such as the alkali ferrates and cupric thiocyanate, were not considered worth-while possibilities, but potassium permanganate was included because of its unique characteristics. Someone may discover how to stabilize it.

The pronounced effect of variations in acidity is shown for solutions such as cupric chloride and bromide and cobalt chloride. Presumably this depends upon the extent to which complex ions are formed. While certain other complexes were included, such as tetrammino cupric sulfate and chloropentammino cobaltic chloride, no attempt was made to exhaust the possibilities among the large number of complex compounds of cobalt or chromium.

While a solution containing trivalent chromium is a desirable green, the system becomes somewhat dichromatic and the hue changes toward the violet on standing, with the ultimate attainment of equilibrium. At the higher acidities, the change is retarded.

As any data obtained for ferric chloride merely corroborated those presented in an earlier report, they are not included here.

Summary

Spectral transmission curves are presented for the visual region for aqueous solutions of ceric sulfate and of various salts of elements from atomic number 23 to 29. These include a considerable range of concentrations and acidities.

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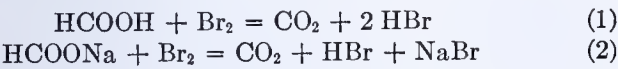
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Determination of Iodine and Bromine in the Presence of Each Other

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IT IS WELL known that bromine is a more powerful oxidizing agent than iodine. Formic acid, for example, is not oxidized by iodine, as is apparent from the nature of Romijn's method for determining formaldehyde (1); bromine, on the other hand, oxidizes not only the acid but also the formates to form carbon dioxide (2) as is indicated in the equations



On the basis of these reactions and the well-known ability of bromine to displace iodine from an iodide, it appeared possible to establish methods (1) for the determination of iodine and bromine in the presence of each other, and (2) for the determination of iodide in the presence of bromide.

1. Sodium formate is added to one aliquot portion of the solution of bromine and iodine; after the bromine has been reduced to bromide, the iodine is titrated with standard thiosulfate solution. Potassium iodide is added to a second aliquot portion of the solution and the total iodine is titrated with thiosulfate solution. The quantity of bromine may be calculated from the difference between the two titrations.
2. The iodide in a mixture of bromides and iodides is liberated by adding bromine; the excess of bromine is reduced by adding sodium formate solution and the iodine is then titrated with thiosulfate.

Experimental

IODINE SOLUTION. Iodine (1.542 grams) was dissolved in 25 per cent potassium bromide solution and diluted to 1 liter with the potassium bromide solution. Ten milliliters of the solution were equivalent to 12.1 ml. of 0.01 *N* sodium thiosulfate.

BROMINE SOLUTION. Bromine (1.052 grams) was made up to 1 liter with 25 per cent potassium bromide solution. Ten milliliters of the solution were equivalent to 13.1 ml. of 0.01 *N* sodium thiosulfate.

POTASSIUM IODIDE. Potassium iodide (1.82 grams) was made up to 1 liter with potassium bromide solution (25 per cent).

SODIUM FORMATE. A 5 per cent solution was prepared from formic acid that had been purified by distillation and from sodium hydroxide of reagent grade. The sodium formate was purified by recrystallization.

Procedure for Bromine in the Presence of Iodine

From 0.25 to 0.35 gram of the substance to be tested is weighed and made up to 250 ml. in a 25 per cent potassium bromide solution. Two 25-ml. portions of this solution are placed in flasks and each portion is diluted to 100 ml. To one of the aliquots is added 1 to 1.5 ml. of the 5 per cent sodium formate solution. The flask is shaken vigorously and then allowed to stand for 10 minutes. The solution is then titrated with sodium thiosulfate solution, using starch indicator. The second aliquot is treated with 5 ml. of 10 per cent potassium iodide solution and then the amount of thiosulfate that is equivalent to the sum of the bromine and the iodine, is determined by titration.

The procedure was tested by preparing mixtures containing from 1 to 20 ml. of each of the halogen solutions. The amount of the sodium formate solution ranged from 0.5 to 2 ml. and the excess of sodium formate from 24 to 82 mg. Each mixture of the bromine and iodine solutions was diluted to 100 ml. A period of 10 minutes was allowed for the interaction of the bromine and the sodium formate in each case. From 2 to 4 ml. of 10 per cent potassium iodide were used prior to titrations for the sum of bromine and iodine. The results are summarized in Table I.

TABLE I. DETERMINATION OF BROMINE AND IODINE IN THE PRESENCE OF EACH OTHER

Iodine Present <i>Mg.</i>	Bromine Present <i>Mg.</i>	0.01 <i>N</i> Thio- sulfate for I ₂	0.01 <i>N</i> Thio- sulfate for Br ₂	Iodine Found <i>Mg.</i>	Bromine Found <i>Mg.</i>
		<i>Ml.</i>	<i>Ml.</i>		
15.35	10.47	12.10	25.15	15.35	10.43
23.02	5.23	18.10	24.65	22.97	5.23
15.35	5.23	12.05	18.60	15.29	5.23
23.02	1.04	18.15	19.45	23.03	1.04
7.67	15.70	6.05	25.65	7.67	15.70
7.67	20.94	6.00	32.25	7.61	20.98
1.53	10.47	1.20	14.25	1.52	10.43

The pH ranged from 3.0 to 6.9, depending upon the amount of bromine present. This variation does not appear to have affected the accuracy of the results.

The presence of sodium formate, even if in tenfold excess over the theoretical amount, does not affect the accuracy of the determination of iodine. The sodium formate must be pure.

Determination of Iodide in the Presence of Bromide

PROCEDURE. From 0.35 to 0.5 gram of the substance to be tested is made up to 250 ml. with water; 25 ml. are pipetted out and diluted to 100 ml.; 10 ml. of 1 per cent bromine dissolved in potassium bromide solution are added; then 2 ml. of 5 per cent sodium formate solution are run in. The mixture is shaken well and allowed to stand for 10 minutes. Finally the iodine is titrated with thiosulfate solution in the usual manner.

The procedure was tested on measured portions of the potassium iodide solution. The iodide content was found from the amount of dried Merck *pro analysi* grade potassium iodide, which had been examined gravimetrically. The excess of bromine added ranged from 91 to 232 mg. and the final excess of sodium formate was from 22.4 to 144.5 mg. The results are given in Table II.

TABLE II. DETERMINATION OF IODIDE IN THE PRESENCE OF BROMIDE

Iodine Present Mg.	0.01 N Sodium Thiosulfate Ml.	Iodine Found Mg.
13.91	10.95	13.81
6.95	5.45	6.91
27.82	21.85	27.79

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Determination of Arsenic in Silver Arsenate

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A METHOD of determining silver by titration with standard potassium iodide in the presence of starch and ceric ions has recently been described (1). This procedure can be extended to the determination of arsenic by means of the above titration after precipitation as silver arsenate and its subsequent solution in nitric acid. This method gives excellent results but cannot be applied in the presence of interfering elements such as phosphorus, vanadium, molybdenum, tungsten, and sexivalent chromium. The precipitation of silver arsenate and the determination of its silver content by the Volhard method is a procedure frequently employed in the analysis of arsenic compounds, particularly arsenic ores (3). The use of the potassium iodide method instead of the Volhard titration eliminates the necessity of frequent standardizations. Standard potassium iodide can be easily prepared by a direct weighing, while the thiocyanate solution must be standardized against pure silver or silver nitrate.

Various methods have been described for the precipitation of silver arsenate from solutions of alkali arsenates. pH control is the important factor; the precipitation will not be complete if the pH is too low, and if too high there will be a co-precipitation of silver oxide. The procedure recommended is that given by Hillebrand and Lundell (2). Because of the solubility of the precipitate in cold water, the procedure was modified by washing with a saturated solution of silver arsenate. When this precaution was not taken the results were consistently low.

Analytical Procedure

From 0.04- to 0.23-gram samples of pure dry potassium dihydrogen arsenate were transferred into 400-cc. beakers. The salt was dissolved in 100 cc. of water and the solution acidulated with nitric acid. To this was added enough 0.1 N silver nitrate to give an excess of approximately 10 cc., and then just enough of a 10 per cent solution of sodium hydroxide to produce a turbidity. Dilute nitric acid was added drop by drop until the solution became clear, and then the silver arsenate was precipitated by the dropwise addition of 10 cc. of a saturated solution of sodium acetate. The solution was heated to boiling to coagulate the precipitate.

After cooling, the solution was filtered and the precipitate washed by decantation with a saturated solution of silver arsenate until a portion of the filtrate gave only a faint opalescence with hydrochloric acid. This opalescence was to be expected because of the silver ions already present in the wash solution. The precipitate was then dissolved from the filter with approximately 30 cc. of warm 2 N nitric acid followed by several washings with hot water. This solution was caught in the beaker in which the precipitation was made. Sufficient 6 N sulfuric acid was added to make the solution about 1 to 2 N with respect to this acid. To this were added 3 cc. of a 0.5 per cent starch solution and 3 drops of an approximately 0.1 N ceric ammonium sulfate solution. The volume before the titration was made ranged from 120 to 150 cc. The solution was titrated with 0.1 N potassium iodide solution to a permanent blue-green end point. A blank titration was made under the same conditions, omitting the silver nitrate.

TABLE I. DETERMINATION OF ARSENIC

KH ₂ AsO ₄ Gram	As ₂ O ₅ Calculated Gram	As ₂ O ₅ Found Gram	Difference Gram
0.0448	0.0286	0.0285	-0.0001
0.0899	0.0574	0.0573	-0.0001
0.1352	0.0863	0.0864	+0.0001
0.1803	0.1151	0.1154	+0.0003
0.2251	0.1437	0.1436	-0.0001

Summary

A method is described for the determination of arsenic in silver arsenate by titration of the silver with potassium iodide, using ceric ammonium sulfate and starch as internal indicators. When the silver arsenate is washed free of silver nitrate with cold water, an appreciable error is introduced due to the solubility of the precipitate. This may be corrected by using a saturated solution of silver arsenate for the washing.

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Determination of Mercury

An Indirect Volumetric Method Based upon a Critical Study and Improvement of the Bichromate-Pyridine Method of Spacu and Dick

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BRIGGS (1) prepared and described pyridine-bichromate complexes of the ions of Cu, Ni, Co, Zn, Mn, Ag, Hg, and U. All these complexes are more or less insoluble.

Spacu and Dick (3) have recommended the precipitation and weighing of mercury as $[\text{HgPy}_2]\text{Cr}_2\text{O}_7$. In their hands this method gave excellent results. It seemed feasible to titrate the dichromate in the precipitate either with a standard reducing agent or iodometrically. Such a titration would have a very favorable factor, since the equivalent of mercury in any titration of this sort is $\text{Hg}/6$. The washing technic proposed by Spacu and Dick has been found to be successful through a compensation of errors, and a less empirical method has been devised for this part of the procedure.

Preparation of Materials

Reagent grade mercuric chloride was used as the material for analysis. Analysis of this salt after drying at 110°C . gave by the method of Spacu and Dick 73.91 and 73.80 per cent of mercury and by the method of Caley and Burford (2) 73.83 and 73.99 per cent. Theory requires 73.88 per cent. The material was accordingly used without further purification.

Merck's "reagent" pyridine and ammonium dichromate of the same quality were used throughout the investigation. It was found more convenient to add 10 ml. of a solution containing 20 grams of ammonium dichromate per 100 ml. instead of 2 grams of the solid salt as recommended by the original investigators. [It is desirable to use pure pyridine of the correct boiling point (115.2°C). Very erratic results may be obtained if the pyridine contains other organic bases.]

Approximately 0.1 *N* solutions of ferrous ammonium sulfate and of sodium thiosulfate were prepared from reagent grade salts and standardized against triply recrystallized potassium dichromate according to established procedures. In the case of the former solution, the standardization was done just before use, and the method of determining the end point was the same as that to be used for the titration of the mercury salt. The potassium iodide used in the iodometric titrations, although slightly yellow in color, gave no color with starch either in neutral or in acid solution.

Two wash solutions were required. The first, used to transfer the precipitate to the filtering crucible, contained 0.5 gram of ammonium dichromate and 0.5 ml. of pyridine per liter; the second, for washing out the above liquid, was made by adding 12 ml. of water to 88 ml. of 95 per cent alcohol. If the gravimetric method is to be used, a third wash mixture containing 1 drop of pyridine per 10 ml. of absolute alcohol is used. The residue of this wash solution is removed from the precipitate prior to weighing by washing with ether.

The indicator solutions were freshly prepared 1 per cent "soluble" starch and 1 per cent diphenylamine in concentrated sulfuric acid.

PRECIPITATION OF MERCURY AS $[\text{HgPy}_2]\text{Cr}_2\text{O}_7$. The precipitation of mercury as $[\text{HgPy}_2]\text{Cr}_2\text{O}_7$ was done exactly as described by Spacu and Dick. The procedure is in brief as follows:

Individual samples of mercuric chloride were weighed into 250-ml. beakers and dissolved in 140 ml. of water. When dissolved, 10 ml. of ammonium dichromate solution were added. The addition of 1 ml. of pyridine to the solution, while stirring it vigorously, precipitated the bright yellow compound which after standing 10 minutes was filtered through a glass crucible. The precipitate was transferred completely to the crucible with the dichromate pyridine solution, and then washed six to eight times with 2- to 3-ml. portions of 80 per cent alcohol to remove the excess dichromate. It is important that the walls of the crucible

as well as the precipitate be washed with this liquid. The crucible was then placed in a drying oven for 15 to 20 minutes to remove the alcohol. Failure to do this always resulted in low values, due to reduction of the dichromate by the alcohol when the precipitate was dissolved in acid. The procedure to this point is common to each of the three volumetric methods.

Conventional volumetric methods for the titration of bichromate were applied after the precipitate had been dissolved. For the potentiometric method with ferrous sulfate and for the iodometric method, 50 ml. of 1.2 *N* hydrochloric acid were used in small portions to dissolve the precipitate; the acid was 2.4 *N* in the other case. The solutions which were titrated with ferrous sulfate contained 20 ml. of 25 per cent phosphoric acid, and the initial volume was approximately 100 ml. Typical results by three methods are presented in Table I.

TABLE I. DETERMINATION OF MERCURY BY TITRATION OF THE SOLUTION OF $[\text{HgPy}_2]\text{Cr}_2\text{O}_7$

Potentiometric Titration with Ferrous Sulfate						
HgCl ₂ present, gram	0.1236	0.2755	0.0871	0.1301	0.1322	0.1952
HgCl ₂ found, gram	0.1235	0.2752	0.0868	0.1300	0.1321	0.1946
Titration with Ferrous Sulfate; 1% Diphenylamine Indicator						
HgCl ₂ present, gram	0.1398	0.1741	0.0875	0.1487	0.1275	
HgCl ₂ found, gram	0.1397	0.1732	0.0872	0.1488	0.1272	
Liberation of Iodine and Back-Titration with Thiosulfate						
HgCl ₂ present, gram	0.0909	0.1138	0.1026	0.1874	0.2263	
HgCl ₂ found, gram	0.0906	0.1137	0.1027	0.1869	0.2261	

Diphenylamine sulfonic acid was also tried as indicator instead of diphenylamine, but the color change was erratic and the end point could not be determined with precision.

USE OF ACETONE FOR WASHING AND DRYING $[\text{HgPy}_2]\text{Cr}_2\text{O}_7$. On the average, results by all methods are somewhat too low. A check of the various steps in the procedure revealed that, even after twenty washings with 80 per cent alcohol, this wash liquid always had a faint yellow tinge, indicating the removal of dichromate from the precipitate. In no case, however, could mercury be detected in these washings with either hydrogen sulfide or stannous chloride. In spite of Spacu and Dick's insistence that the complex compound is insoluble in all wash liquids recommended, a steady loss of weight was observed each time the precipitate was washed with 80 per cent alcohol:

First weight of precipitate, gram	0.2750	0.3072
After 7 more washings, gram	0.2741	0.3062
After another 7 washings, gram	0.2733	0.3055

The density of the alcohol agreed with that given in the original paper; the solution was only slightly acid, showing a pH of approximately 6 with nitrazine paper. To determine whether the slight acidity might be responsible for the solubility of the compound, some alcohol was left standing over calcium oxide for 20 hours and then distilled from the oxide. This was diluted to a specific gravity of 0.849 with boiled water. The washings with this liquid were still yellow, however, even after fourteen washings. The addition of a drop of pyridine to 10 ml. of the alcohol did not decrease the yellow tint of the washings. The results with 95 per cent alcohol were no better.

Acetone, on the other hand, apparently dissolved the compound only to a slight extent, for the washings showed no

color. The following weights of precipitate were obtained on successive washings:

Initial weight, gram	0.5627	0.3675
After 6 washings with acetone, gram	0.5625	0.3672
After 6 more washings, gram	0.5625	0.3671
After 6 more washings, gram	0.5624	0.3671

The greater difference between the first and second weights may in part be due to the condensation of moisture on the crucible while the weights were being adjusted; in subsequent weighings the weights were placed on the pan of the balance before removing the crucible from the desiccator. But even disregarding this possibility, it is evident that the compound is much less soluble in acetone than in 80 per cent alcohol. The use of acetone has several advantages over the series of wash liquids recommended by Spacu and Dick. It removes the adhering ammonium dichromate as readily as the alcohol, and since acetone is almost as volatile as ether, the use of absolute alcohol and ether is unnecessary when the gravimetric method is used. The procedure adopted was to wash six to eight times with ordinary acetone after the precipitate had been transferred and washed with the ammonium dichromate-pyridine solution. Air was then drawn through the crucible for 5 minutes to evaporate the acetone, after which the crucible was wiped with a clean cloth and placed in a vacuum desiccator for 10 to 15 minutes. Gravimetric and iodometric results when acetone was used as a final wash liquid are shown in Table II. These results are not as superior to those obtained with the alcohol wash as had been expected. It may be that in the presence of the dichromate which adheres to the precipitate little or none of the precipitate dissolves and that the six to eight washings recommended are just sufficient to remove this excess completely without dissolving any ap-

preciable quantity of the precipitate. Such an assumption would account for the excellent results reported by Spacu and Dick. It appears, however, that acetone is the more advantageous wash liquid, if for no other reason than that by its use three washing mediums may be replaced by one.

TABLE II. RESULTS WITH ACETONE

HgCl ₂ Taken Gram	Weight of [HgPy ₂]Cr ₂ O ₇ Gram	HgCl ₂ Found (from col. 2) Gram	Volume of 0.0975 N Na ₂ S ₂ O ₃ Ml.	HgCl ₂ Found (from col. 4) Gram
0.1443	0.3057	0.1444	32.76	0.1445
0.1792	0.3785	0.1788	40.53	0.1788
0.1619	0.3421	0.1616	36.69	0.1619
0.1579	0.3338	0.1577	35.69	0.1575
0.2654	0.5625	0.2657	60.07	0.2650
0.1733	0.3672	0.1735	39.25	0.1732

Summary

Mercury may be determined indirectly by precipitating [HgPy₂]Cr₂O₇ and titrating the dichromate in the precipitate. The titration may be effected iodometrically or with ferrous sulfate, either potentiometrically or with diphenylamine as indicator. The importance of the use of pure pyridine is emphasized. The substitution of acetone for the wash liquids previously proposed simplifies and improves the washing technic.

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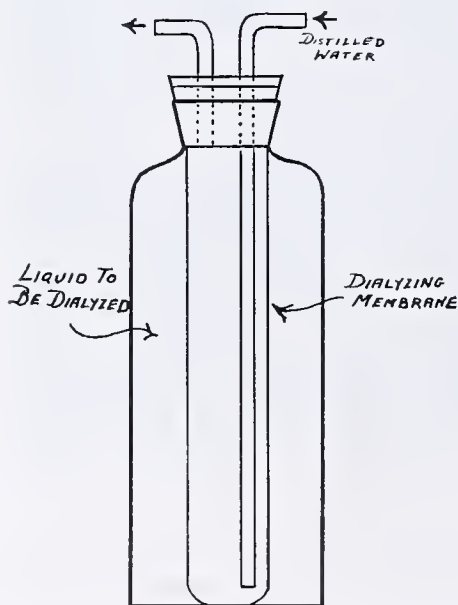
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A Constant-Volume Dialyzer

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CONSTANT-volume dialyzers previously described are of two main types. The first is the "pressure dialyzer" (1), while the second involves the "evaporation method" technic which depends upon evaporation to maintain (or attain) the original volume. A weakness of the first lies in the fact that the final volume is usually found to have increased, as it is difficult to fill the dialyzing sac initially to the distended condition it attains at the end of the dialysis. The second method may be criticized because deposited material on the sides of the container may become irreversible; and because of the effect of atmospheric gases, and of temperature if heat is used as an aid in evaporating. The



latter point is frequently overlooked, although it is well known that many metal oxide hydrosols undergo extensive changes upon heating (2-5).

To overcome these difficulties, a simple and practical constant-volume dialyzer has been developed in these laboratories. Details are shown in the figure.

A bottle of the type illustrated is fitted with a two-hole rubber stopper. A membrane, wide enough to fit tightly over the stopper chosen and long enough just to touch the bottom of the bottle when the stopper is tightly inserted, is used. Through the rubber stopper pass an inlet tube extending to the bottom of the dialyzing sac, and an outlet tube. The liquid to be dialyzed is placed in the bottle, the distended membrane, filled with distilled water supplied from a source 3 feet above the table, is inserted, and the bottle is tightly stoppered. Care should be taken to exclude air bubbles. Distilled water is then passed through the dialyzing tube at any desired rate.

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The Particle Size of Insecticidal Dusts

A New Differential Manometer-Type Sedimentation Apparatus

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THE determination of the particle size of finely divided materials by sedimentation analysis has been carefully investigated by Odén (3, 6, 7). The method is based on Stokes' law, which gives the relation between the velocity of a particle and its radius when falling in a fluid medium under the influence of a constant force, usually gravity. He obtained a curve by plotting the weight of accumulated sediment as ordinate against time as abscissa and from this the particle size and particle-size distribution were calculated. Although not the first to use Stokes' law in this connection, Odén contributed the graphical method for the determination of particle-size distribution from the accumulation curve. A condensed report of the extensive researches by Odén and others on this subject is given in Alexander's "Colloid Chemistry" (7).

Instead of measuring the weight of sediment accumulated, Wiegner (9) measured the decrease in the density of the suspension with an apparatus that would be very similar to the one shown in Figure 1 if all parts above the center stopcock, *F*, were removed. The large tube contained the suspension and the small manometer tube the suspending liquid. Since the density of the suspension is greater than that of the pure liquid, the meniscus in the manometer tube will stand at a higher level than that in the sedimentation tube. As the particles settle and pass the opening to the stopcock, *D*, their effect on the density is lost and the difference in the level between the two columns gradually decreases.

It is not desirable to use a suspension containing more than 1 per cent of solids (10 grams per liter) in any sedimentation analysis. If this concentration is used, it is evident from a simple calculation that the rise in Wiegner's manometer tube will not exceed 1 cm. even for the most dense materials. Kelly (5) has magnified this movement in the manometer tube by having it nearly horizontal at the top, so that a slight change in level causes a large movement of the meniscus. Evaporation and the difficulty of adjusting the level of the suspension, as well as the position of the tube itself, are serious disadvantages. Gessner (4) has magnified the rise in Wiegner's apparatus photographically and recorded the change on a photographic paper attached to a revolving drum. Even with this arrangement it is necessary for him to use a 5 per cent suspension to obtain a suitable change. Moreover, the apparatus is complicated and must be used in a dark room. A differential manometer has been used by Crowther (2) and by Puri (8) in studying the sedimentation of soils, but their type of manometer and the construction of their instruments are different from the one developed in this laboratory.

A new type of sedimentation apparatus is described which employs the principle of the differential manometer. A movement of the meniscus in the manometer corresponding to a change in concentration of 50 mg. per liter in the suspension can easily be detected without optical magnification.

The density of the dispersed substance can be determined directly in the apparatus with sufficient accuracy to be used in the calculation of particle size, at least for dusts that do not vary greatly in particle size.

Dilute ethyl alcohol near the concentration having maximum viscosity is recommended as the most satisfactory sedimentation medium for insecticides in this apparatus.

The sedimentation apparatus to be described here employs the principle of the differential manometer, using two immiscible liquids. By this means the rise obtained can be increased to 50 or 100 times that obtainable in the manometer of Wiegner's apparatus, and the decrease in density of the suspension can be measured accurately. A movement of the meniscus in the manometer corresponding to a change in density of 0.00002 gram per cc. can easily be detected without the aid of optical magnification. This change in the density of the suspension corresponds to a change in concentration of about 50 mg. per liter when the dust has a density of 3.0 grams per cc.

From the density of the suspension, d_s , the suspending medium d_m , and the top liquid, d_t , together with the settling height, H , the following equation can be derived to calculate the rise, R , in the manometer produced by a suspension of dust:

$$R = \frac{H(d_s - d_m)}{(d_m - d_t)} \quad (1)$$

From this equation it is evident that R can be increased either by increasing the concentration of the suspension or by decreasing the difference in the densities of the two liquids. Practically there is a limit to both of these variations.

Description of Apparatus

The apparatus, shown in Figure 1, is made from standard Pyrex tubing. The large tube, *A*, is 50 cm. long by 4.5 cm. in diameter. A smaller tube, *C*, about 2.5 cm. in diameter, extends the total length to 86 cm. The jacketed manometer tube, *B*, 4-mm. inside diameter, is joined through a 3-mm. bore stopcock, *D*, 13 cm. from the bottom of the large tube and again through a similar stopcock, *E*, 8 cm. from the top of the apparatus. A scale, *S*, is inserted behind the upper half of the manometer tube inside the jacket. The jacket protects the delicate manometer tube and when evacuated reduces the effect of rapid changes in temperature. The 2-mm. stopcock, *F*, is used to set the level of the suspension.

The construction around stopcocks *D* and *E* is important. They should be not more than 2 cm. from the large tubes, and the connecting tube must be blown out large and cone-shaped. This prevents the entrapment of bubbles at *D* and decreases the amount of sediment that settles there. The tube connecting stopcock *E* should drain and fill easily to the plug in the stopcock.

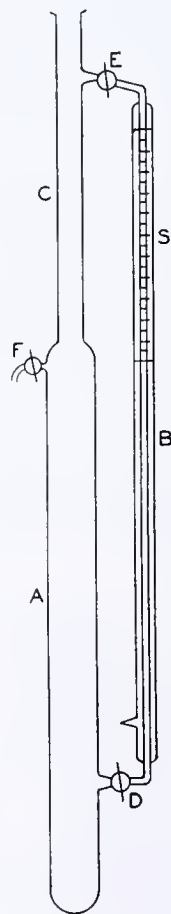


FIGURE 1. APPARATUS

A slightly oblique angle in the upper tube between the stopcock and the end of the manometer tube is also important.

Choice of Liquids

The choice of liquids to be used in this apparatus depends largely on the sedimentation medium that is suitable for a particular material. The physical or chemical nature of either the dispersed dust or the dispersing medium must not

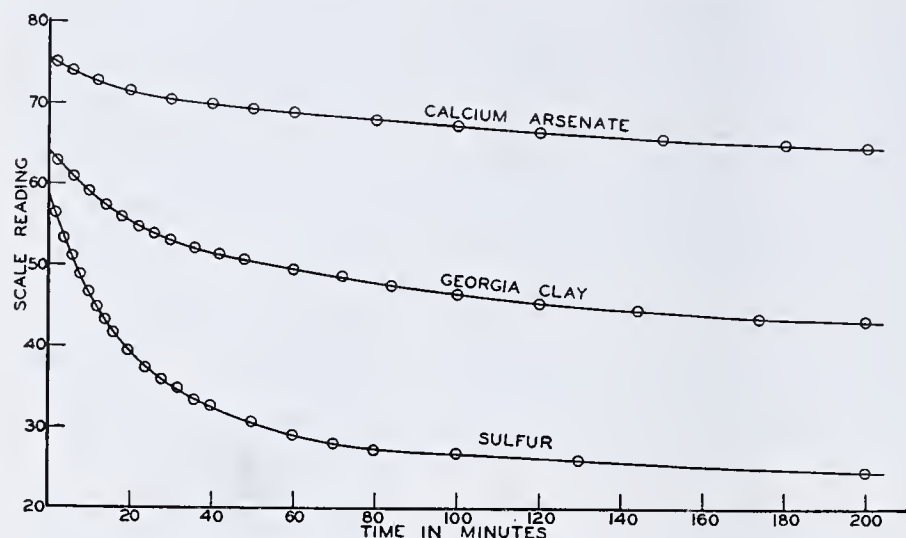


FIGURE 2. MANOMETER READINGS

change when the suspension is prepared. Fortunately many insecticides can be suspended in water, alcohols, or mixtures of these liquids without appreciable solution or reaction. Water alone and some alcohol-water mixtures were tested in this apparatus.

The next problem was to find an upper liquid that was immiscible with the sedimentation medium, and had a slightly lower density. It is usually more convenient to use a mixture adjusted to the proper density rather than to search for a pure liquid. A mixture of hydrocarbons adjusted to the proper density by the addition of chlorinated compounds was used with the sedimentation media mentioned above.

It is very important that the sedimentation medium and the upper liquid have a very low mutual solubility. A movement of one liquid phase into the other interferes with the sedimentation by changing the nature and density of the medium. A small change in the density of either liquid also introduces a large error in the manometer readings on this sensitive instrument. The mutual solubility of the liquids can be checked by running a blank determination. In this case the manometer reading corresponds to the point of complete settling of the suspension during a regular run. The ideal pair of liquids would give a stable zero reading which would not change, at least, during the time required for a sedimentation analysis. This is nearly attained with the pair of liquids described below, which are recommended for use in this apparatus in the analysis of many insecticides.

Dilute ethyl alcohol made by mixing equal volumes of water and 95 per cent alcohol was found to be a suitable sedimentation medium. As this mixture is approximately 50 per cent by volume, it will be referred to as such. The density is 0.9280 gram per cc. and the viscosity is 0.02346 poise at 25° C., although these values vary slightly with different lots of alcohol.

This medium has several advantages. Because of its low surface tension, no foaming occurs and there is no interference with the movement of the meniscus in the manometer. While the solubility of many inorganic salts is lower in 50 per cent alcohol than in water, thus decreasing the action of electrolytes, this mixture is still capable of dissolving many

of the common deflocculating agents. Another important factor is its relatively high viscosity. The maximum viscosity for an alcohol-water mixture occurs near the 50 per cent point and is about three times that of either component. A substantial shortening of the sedimentation tube is therefore possible without sacrificing accuracy in the coarse fractions.

The top liquid is made by adding 1,2,4-trichlorobenzene to decahydronaphthalene to obtain a density of about 0.9000 gram per cc. A small amount of an intensely colored oil-soluble dye is added, and the mixture is extracted three times with a slightly ammoniacal 50 per cent alcohol solution. This extraction removes soluble substances in the upper liquid and saturates it with dilute alcohol. If an emulsion persists in the oil layer, it may be removed by filtering through a fluted paper. The solution is then adjusted to a density of 0.9000 ± 0.0002 gram per cc. by adding more 1,2,4-trichlorobenzene. About 100 cc. are used for each determination. A liter or two of this liquid is sufficient, since it can be recovered and used again after the density has been adjusted.

Control of Temperature

A differential manometer with arms of unequal diameter is very sensitive to changes in temperature. The apparatus must therefore be operated at some constant temperature, or under conditions where the change in temperature is very slow. A room varying not more than 0.5° per hour is satisfactory, but a water bath regulated at a definite temperature is better. A controlled water bath simplifies the calculations, but a slightly different technic must be used. The upper part of the water bath must be provided with a glass window, and the suspension must be stirred by a plunger without removing the apparatus from the bath. This eliminates the cooling effect caused by evaporation from the wet apparatus when it is shaken outside the bath. A long-handled brush saturated with dilute alcohol served as an excellent stirrer. Not less than 50 rapid strokes are necessary to obtain a uniform suspension. A correction can easily be applied for the amount of sample removed on the brush.

Procedure

The following detailed procedure for the determination of the particle-size distribution of a Georgia clay may be used with slight variations for many other materials.

A 7-gram sample was mixed to a thick paste with 50 per cent alcohol to which had been added 5 drops of ammonium hydroxide (sp. gr. 0.90). After the lumps had been broken up and a smooth paste obtained, more 50 per cent alcohol (50 cc.) was added and the sample shaken overnight.

The apparatus, especially the manometer tube, was carefully cleaned and rinsed with 50 per cent alcohol. It was then filled to the stopcock, *F*, with the sedimentation medium (about 600 cc.), and from 3 to 6 drops of concentrated ammonium hydroxide were added. After a thorough mixing, the manometer tube was filled by tilting the apparatus and the stopcocks were closed. Some of the dilute alcohol was poured out and the previously dispersed sample introduced. The alcohol was used to wash in remaining portions of the sample, and finally the level was adjusted by adding sufficient liquid to overflow at *F*. The suspension was then thoroughly mixed and placed in the water bath until it reached 25° C., the temperature of the bath.

After about 20 minutes the suspension was again thoroughly stirred with a long-handled brush or plunger, and the top liquid was added through a long-stemmed funnel having several fine holes in the side of the stem near the bottom instead of one large hole in the end. With this device the liquid was sprayed against the sides of the apparatus, so that it flowed down gently without disturbing the upper layer of the suspension. The top liquid must also be at the same temperature as the bath. The stop-

watch was started immediately after the last stirring, but it was returned to zero after 30 seconds because settling does not start until the eddy currents die out. About 45 seconds are required to introduce the top liquid and open the two stopcocks on the manometer. The upper liquid rapidly replaces the dilute alcohol in a part of the manometer tube and equilibrium is reached in about 2 minutes. A reading can be obtained at 1 minute, but this point is usually above the curve.

The zero point, or the point denoting complete settling, was found to be 20 on the manometer scale. It was obtained by running a blank determination. It is neither practical nor necessary to continue the readings to this point.

Results

The readings obtained for the Georgia clay are presented in Table I, together with the readings for a run on samples of dusting sulfur and calcium arsenate. In Figure 2 these data are plotted to show the type and regularity of the sedimentation curve.

The particle-size distribution for some fractions is presented in Table II. The amount falling in each fraction was determined by the graphical method of Odén.

The results of a sedimentation analysis may be expressed in several ways. Borchers and May (1) suggest the use of the sedimentation curve with a table giving the particle-size distribution, as has been done above. The distribution may be expressed graphically as an accumulative frequency curve or as a frequency-distribution curve. Since this paper is concerned primarily with the use of a new apparatus, it is not considered necessary to present the distribution graphically.

After a little experience the sedimentation curve itself will give considerable information. A curve with a rapidly changing slope indicates a polydispersed sample, while a curve approaching a straight line indicates monodispersion. Unless two samples have approximately the same particle-size distribution, it is possible to pick the finer material without further calculation. The curves also give a graphical comparison of the densities. The material whose extrapolated curve intersects the zero ordinate at the highest point has the highest density. This point is of practical importance, as shown below.

Determination of Density

Since the rise in the manometer can be calculated from the density of the suspension (Equation 1), then conversely the density of the suspension, and hence the density of the dust, can be calculated from the rise. The rise can be obtained by extrapolation of the sedimentation curve and from the determination of the zero point. Therefore

$$\frac{R}{H} (d_m - d_i) = d_s - d_m = \Delta d \tag{2}$$

After Δd is obtained in this manner, the density of the dust can be calculated from the following formula:

$$\frac{d_m C}{C - \Delta d} = D$$

where C is the concentration of the dispersed phase in grams per cubic centimeter of suspension and D is the density of the dispersed phase.

The precision obtainable by this method is about 0.1 unit in density. For dusts that settle slowly, or that do not vary greatly in particle size, this error in density will shift about 1 per cent or less from one fraction to another. For dusts that vary greatly from some mean particle size, as in the case of the sulfur sample reported here, a shift of about 4 per cent is obtained on some of the larger fractions. For the first type of dust this method of density determination is

considered sufficiently accurate for the calculation of particle-size distribution, and it may be used in the second case if the error introduced falls within the limits of accuracy desired.

Table III shows the densities of the three insecticides under discussion when obtained with the sedimentation apparatus, as compared with the values obtained in a pycnometer.

TABLE I. MANOMETER READINGS AT DIFFERENT TIMES FOR THREE TYPICAL INSECTICIDAL MATERIALS

Time Min.	Manometer Scale Readings		
	Georgia clay	Calcium arsenate	Dusting sulfur
1	67.0	78.0	67
2	62.8	74.8	56.3
4	61.7	74.2	53.3
6	60.8	73.9	51.0
8	59.9	73.4	48.8
10	59.0	73.0	46.7
12	...	72.7	44.8
14	57.3	...	43.2
16	...	72.0	41.7
18	55.9	...	40.5
20	...	71.4	39.4
22	54.6
24	37.4
26	53.8
28	36.0
30	53.0	70.4	...
32	34.8
36	52.1	...	33.6
40	...	69.8	32.6
42	51.3
48	50.7
50	...	69.2	30.7
60	49.5	68.8	29.1
70	28.1
72	48.6
80	...	67.9	27.3
84	47.5
100	46.5	67.2	27.0
120	54.4	66.4	...
130	26.2
144	44.7
150	...	65.7	...
174	43.7
180	...	65.1	...
200	42.8	64.7	24.8
220	24.4
240	...	63.7	...
320	...	61.6	...

TABLE II. PARTICLE-SIZE DISTRIBUTION OF THREE TYPICAL DUSTS

Material	Percentage (by Weight) of Material of Indicated Range of Radii				
	Above 20 μ	20-10 μ	10-7.5 μ	7.5-5 μ	Below 5 μ
Calcium arsenate	1	2	3	6	88
Dusting sulfur	16	38	19	4	23
Georgia clay	1	12	10	9	68

TABLE III. COMPARISON OF DENSITIES OBTAINED ON THE SEDIMENTATION APPARATUS WITH THOSE DETERMINED IN A PYCNOMETER

Material	By Pycnometer		By Sedimentation Apparatus
	In 95 per cent alcohol	In 50 per cent alcohol	
Calcium arsenate	3.25	...	3.23
Dusting sulfur	...	2.07	1.93
Georgia clay	2.52	...	2.43

Discussion

The most desirable form of this apparatus would be one that could be used in any laboratory without special precautions against changes in temperature. With this in mind a tube was constructed having the manometer inside the large tube. As far as the manometer was concerned, the temperature effect was almost eliminated, but rapid changes in temperature also cause eddy currents in the suspension which interfere with normal sedimentation. For coarse materials this error is small, and further efforts are being made to develop a satisfactory apparatus according to this principle.

An apparatus similar to that shown in Figure 1, but pro-

vided with a jacket through which water could be circulated, was also tried. This requires some means of circulating water at constant temperature. No advantage is gained over the use of the simple design in a water bath.

The accuracy attainable with the apparatus is subject to the same criticism as that of any method of sedimentation analysis. The shape of the particle and the lack of complete dispersion, partial flocculation, etc., have been discussed at length by other authors. It is felt, however, that the advantages over the microscopic or air-elutriation methods, as pointed out by Borchers and May (1), are sufficient to justify the use of sedimentation analysis, especially for technical purposes. The precision obtainable with this instrument is dependent upon the accuracy with which the tangents to the sedimentation curve can be drawn. Actual

readings taken on the manometer during carefully conducted check runs do not vary more than 2 per cent.

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A Variable Vapor-Volume Barometric Type of Vapor Pressure Apparatus

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IN MANY problems involving the use of gasolines, naphthas, and similar volatile products it is desirable to know the vapor pressure of these products over the initial range from zero to some intermediate per cent evaporated. In connection with several problems requiring this type of information, a variable vapor-volume barometric type of vapor pressure apparatus, which gives somewhat more detailed and accurate information than the usual Reid vapor pressure test and yet is sufficiently rapid in operation to allow its use for semi-routine testing, has been used by the writers with considerable success.

It is the purpose of this paper to describe briefly the design and operation of this apparatus and to indicate the manner in which the results obtained from it may be applied to several typical problems, particularly to the measurement of evaporation losses and the vapor-locking characteristics of gasolines.

Design of Apparatus

The apparatus, which consists essentially of two glass tubes joined at the bottom to a leveling bottle, is illustrated in Figures 1 and 2. The long glass tube, A, is 220 cm. long, has a scale graduated in millimeters over 200 cm. of its length, and is open

to the atmosphere at the top. The tube, B, is sealed off at the top with a large carefully ground three-way stopcock and has alternately long narrow sections 30 cm. long and 1 cm. in diameter to obtain accurate readings of the liquid volume, and bulbous sections 15 cm. long and 3 cm. in diameter to accommodate a relatively large vapor volume.

The open tube, the buret, and the leveling bottle, which constitute the essential parts of the vapor pressure measuring system, are filled with mercury, and in order to obtain temperature control are immersed in a water bath at 37.8° C. (100° F.). The bath is thermostatically controlled and has a temperature gradient of 0.05° C. (0.1° F.) from top to bottom and a variation in the average of about 0.1° C. (0.2° F.).

Readings are made by means of a cathetometer which clamps to the tie rod at the front of the apparatus and is adjusted between the meniscus level and fixed stations on the tube and buret by means of a 40-thread micrometer screw. Successive trial measurements between two fixed points indicate that the settings of the cathetometer hair lines can be reliably reproduced to about ± 0.004 ml. in sections 1, 3, and 5. A bright light behind the apparatus silhouettes the meniscus levels and greatly facilitates the setting of the cathetometer cross hairs.

Operation of Apparatus

Preliminary to running each test, the mercury level is dropped below the air injector, D, and with the stopcock opened to the

TABLE I. RESULTS OF REPRESENTATIVE TEST

(Sample 131.8)

Mercury ^a Level	Mercury Level ^b Corrected	ΔP^c	Vapor ^d Pressure	Barometer	Vapor Volume Observed ^e	Vapor Volume Corrected ^f	Liquid ^g Volume	Evaporated ^h	V/L ⁱ
Mm.	Mm.	Mm.	Mm.	Mm.	Cc.	Cc.	Ml.	%	
508	358	351	157	599	7.1	5.6	10.008	0.31	0.56
552	397	390	162	594	9.1	9.1	10.000	0.39	0.72
795	502	501	294	462	76.0	46.2	9.800	2.51	4.73
1024	711	704	320	436	120.7	68.7	9.665	3.72	7.10
1131	813	806	325	431	128.2	72.8	9.643	3.94	7.56
1261	918	917	344	412	178.5	96.8	9.500	5.24	10.20
1503	1141	1134	369	387	240.3	122.4	9.373	6.64	13.00
1523	1159	1152	371	385	241.6	124.0	9.364	6.72	13.29

^a Values, given as mm. of mercury, are obtained by direct observation of mercury levels in tubes.

^b Column 2 corrected for height of column of gasoline. When approximately 10-cc. sample is used, subtract 7 mm. in sections 1, 3, and 5; 1 mm. in sections 2 and 4.

^c Difference in mercury levels: column 1 - 3; or column 1 - 2 corrected.

^d Vapor pressure = barometric pressure (column 6) - ΔP (column 4).

^e Volume of vapor above gasoline.

^f Corrected to 760 mm. = observed vapor volume $\times \frac{VP}{760 \text{ mm.}}$, 37.75° C. (100° F.).

^g Volume of liquid gasoline = volume between meniscus levels + volume included in meniscus (1, 2; Figure 3). Original volume, 10.045 ml.

^h Per cent evaporated = $\frac{\text{initial volume} - \text{liquid volume}}{\text{initial volume}} \times 100$.

ⁱ Vapor-to-liquid volume ratio = vapor volume (column 8) \div liquid volume (column 9). At 37.75° C. (100° F.), 760 mm.

atmosphere, air is blown through the buret to rid it of any vapors from the previous test. The mercury is then raised to the top of the buret, the stopcock closed, and the leveling bottle dropped until a vacuum of almost one atmosphere can be sustained. This procedure appears to be effective in freeing both the buret and the mercury from gases and volatile impurities.

Following these preliminaries, the mercury level is again raised and the stopcock opened to the sample bottle. The required volume of sample is then displaced into the buret by gradually lowering the mercury level and simultaneously pushing the sample by a slight pressure head from the water bottle (Figure 2). When the sample has been obtained in this manner, the stopcock is sealed off and the sample is allowed to stand for several minutes to reach the temperature of the bath. After this condition is attained the mercury level is dropped until some of the sample has evaporated. The barometric pressure, the vapor and liquid volumes, and the mercury levels are then recorded and the vaporization is repeated in successive increments to the bottom of the buret. Readings are, of course, taken after each increment of vaporization.

After each increment of vaporization a period of 10 to 12 minutes was allowed before readings were taken, so as to permit a close approach to equilibrium between the liquid and the vapor.

It is believed that this period was sufficient to ensure approximately equilibrium vaporization, since allowing a period of as much as 6 hours in several cases produced an additional change of only 1 to 2 mm. in the vapor pressure.

When very accurate liquid volume measurements are required, as in measuring small evaporation losses (0.5 per cent and less) it is necessary to read the height of the meniscus and apply a correction for the volume of liquid that is contained in it (7, 8). This correction, shown in Figure 3 for the buret used in this work, normally ranges from 0.02 to 0.05 ml. and introduces no complication, as it is simply an additive correction to be applied to the liquid volume measurement.

Table I gives the observations and the computation of the results for a representative test on a gasoline sample, and Figure 4 is a plot of the results for this sample test. All the calculations are simple arithmetic and can be carried out by the operator in the short periods of waiting for equilibrium after each successive increment of vaporization.

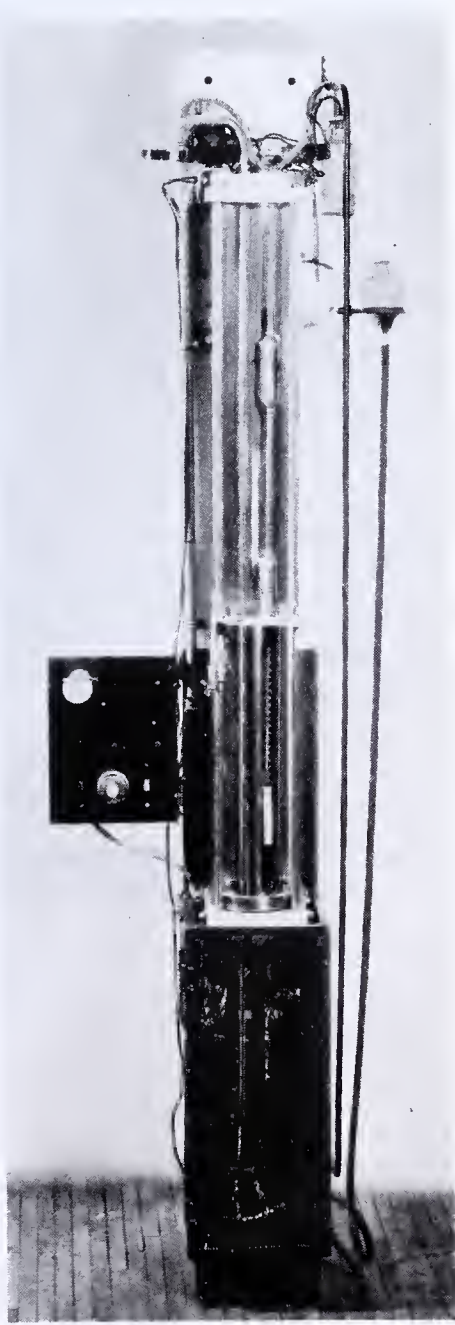


FIGURE 1. APPARATUS FOR MEASUREMENT OF EVAPORATION LOSSES

SCHEMATIC DIAGRAM OF VAPOR PRESSURE APPARATUS

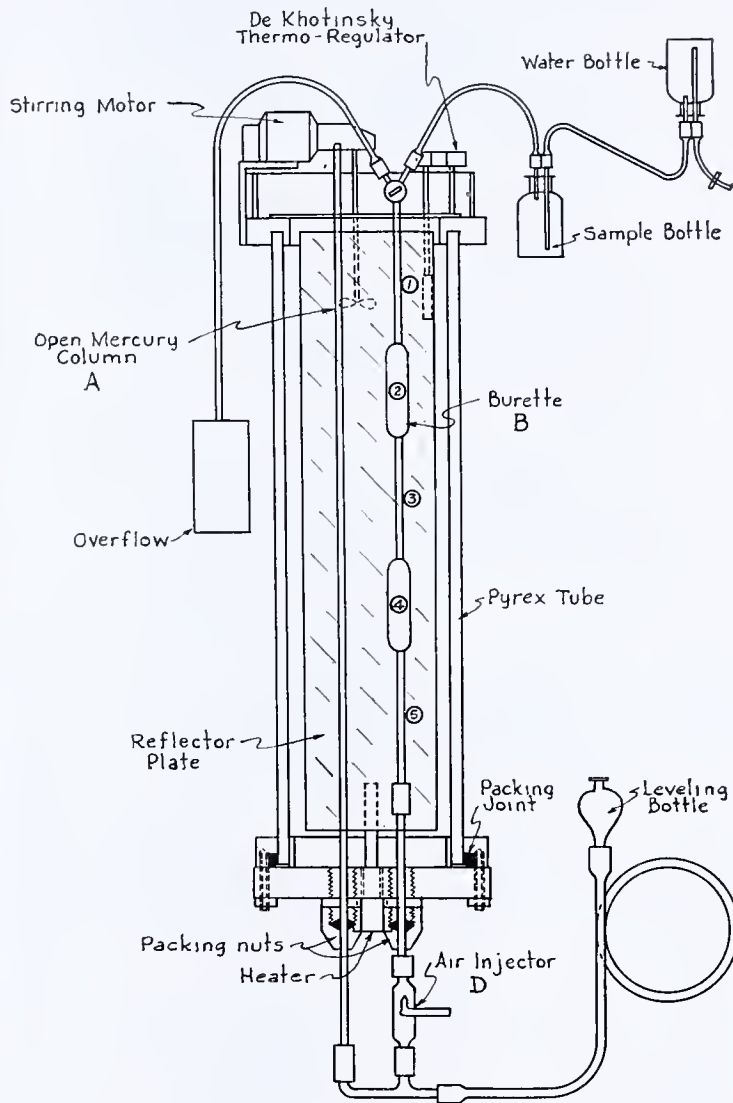


FIGURE 2

Using this apparatus and procedure an operator can, barring accidents, run about six samples in an 8-hour day. In running samples where evaporation losses are very small (0.5 per cent or less) and very accurate curves are required, four samples a day are about average. In other cases less care is required and six or eight samples are usually handled.

Preliminary Tests with Apparatus

Among the first tests made with this apparatus was a series of preliminary runs to determine (1) the agreement of measured vapor pressure values with accepted standard values for a series of pure compounds, and (2) the accuracy with which the values on one product could be reproduced in successive tests.

VAPOR PRESSURES OF PURE COMPOUNDS. Table II gives the vapor pressure values of cyclohexane, benzene, chloroform,

TABLE II. VAPOR PRESSURES OF PURE COMPOUNDS

Material Tested	Vapor Pressure by Apparatus Mm.	Test Temperature ° C.	Test Temperature ° F.	Vapor Pressure Given by International Critical Tables Mm.	Preparation
Cyclohexane	170	37.75	100	168	c. p. material redistilled and middle cut taken
Benzene	172	37.83	100.10	173 (6)	Same
Chloroform	340	37.83	100.10	338	Same
Carbon disulfide	574	37.75	100	574	Same
Water	50	37.75	100	48.9	Distilled

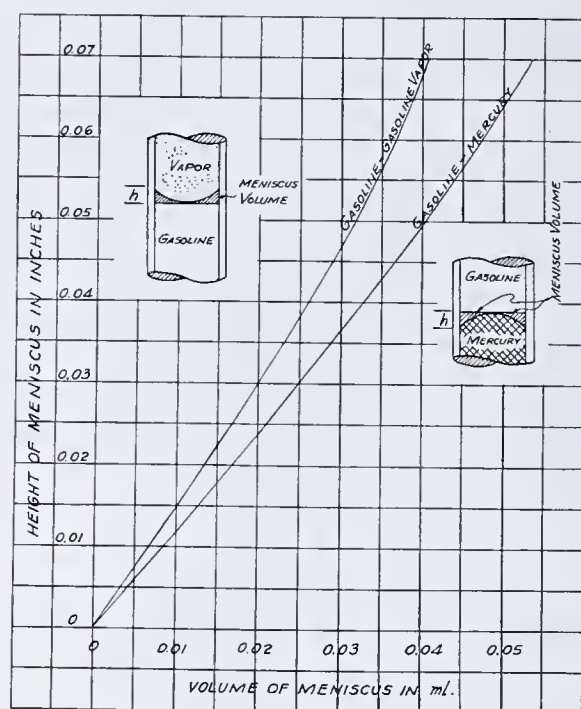


FIGURE 3. CORRECTION FOR VOLUME OF MENISCUS

For use in sections 1, 3, and 5 of vapor pressure apparatus. Both corrections are added to gasoline volume.

carbon disulfide, and water, determined at a temperature of 37.8° C. (100° F.) in this apparatus. For comparison, the "standard values" for the vapor pressure of these products, obtained by interpolation in the vapor-pressure tables in the International Critical Tables (3), are also given. It will be noted that 2 mm. is the greatest discrepancy between the experimental and accepted values.

In making these tests, the procedure of running a curve of vapor pressure versus vapor-to-liquid volume ratio and per cent evaporated was followed. Despite the care taken in purifying these materials, a slightly high value of the vapor pressure was noted with very small amounts evaporated in the case of all the materials except water. However, as the amount evaporated was increased, the vapor pressure values quickly approached the steady values reported in Table II. As these high initial vapor pressures were considered to indicate the presence of small quantities of volatile impurities and as it was necessary to carry the evaporation furthest in the case of the least pure material, it is suggested that this apparatus might offer a quick and simple means of estimating the amount of volatile impurities in supposedly pure compounds.

ACCURACY AND REPRODUCIBILITY OF TEST. A series of curves of vapor pressure versus vapor-to-liquid volume ratio and per cent evaporated were run all on the same gasoline sample in order to obtain a reasonably reliable figure by which to judge the reproducibility of subsequent tests. In the first attempt to run this series of tests the following interesting though accidental results were obtained:

A 500-ml. sample of the gasoline for test was poured into a sample bottle which was subsequently connected to the buret as shown in Figure 2; and when successive portions of this sample were run into the buret and tested, curves 2, 3, and 4 of Figure 5 were obtained. As these tests showed a very disappointing spread, the operation of the next test was watched carefully to determine if possible the reason for this variation.

While watching this test it was noticed that after the sample was displaced into the buret, the water bottle was placed base up (inverted posi-

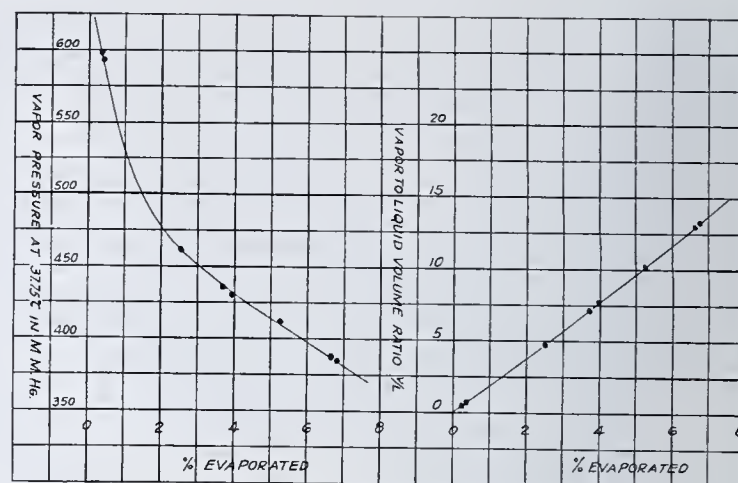


FIGURE 4. RESULTS OF SAMPLE TEST, TABLE I

tion of that shown in Figure 2) on a ledge slightly below the sample bottle. This tended to siphon some of the water from the bottom of the sample bottle back into the water bottle and allowed vapor to form to a depth of about 3 cm. at the top of the sample bottle. After this test, from which curve 5 of Figure 5 was determined, a new sample was taken and curve 1 was determined. In taking this second sample the gasoline was displaced from the main storage into the sample bottle and thence into the vapor pressure apparatus in such a way that no vapor formed at any time during the transfer.

The difference between curves 1 and 2 (corresponding to about 1 per cent loss) was attributed to the displacement loss of pouring the first sample into the sample bottle and the difference in curves 2, 3, 4, and 5 to the small vapor loss that occurred each time the water bottle was inverted.

These accidental results serve to illustrate the importance of careful sampling and handling of volatile materials and also to indicate the sensitivity of the apparatus.

As a result of these tests all samples were handled by water displacement and for this purpose two-hole rubber stoppers with two glass tubes in them are sealed into pint wide-mouth bottles. One glass tube extends just through the stopper flush with its inside edge and the other extends almost to the bottom of the bottle. The bottle is filled with water and the sample is displaced into it at the time of sampling and out of it into the buret at the time of test.

Curve 1 of Figure 5 was subsequently verified by several additional runs in which the samples were all handled by the method just described and, as it was impossible readily to

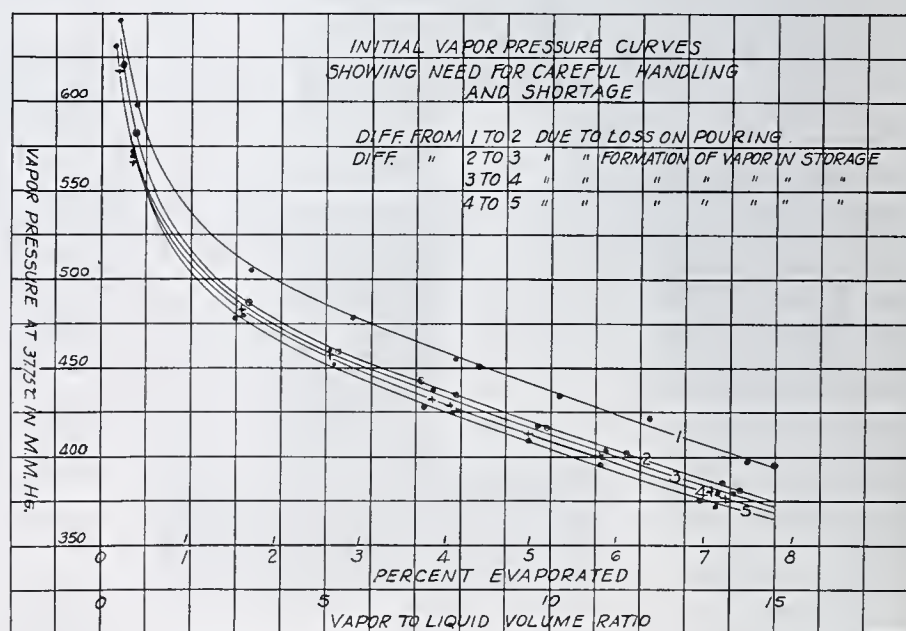


FIGURE 5

distinguish the curves for the separate runs when the plots of them were superimposed, the following method was used for the comparison of the results:

The equation of the curve determined by each individual run was developed by the method of averages (4) for all points above 1 per cent evaporated and the separate equations were solved to determine the vapor pressure at a common per cent evaporated. The results of these tests and calculations indicated a probable (50 per cent) error of about 1 mm. of mercury and a maximum range of about 3 mm. of mercury. This method of comparing the results was felt to be the most justifiable one, since in all cases the average curve through the points is the result that is of interest.

Application to Typical Problems

ESTIMATION OF EVAPORATION LOSSES. Stauffer, Whitman, and Roberts (9) have suggested that evaporation losses can be estimated accurately by determining a curve of vapor pressure versus per cent evaporated on samples of the product both before and after the occurrence of the evaporation loss. In this method the loss is measured as the difference in per cent evaporated at a value of the vapor pressure common to both the weathered and unweathered samples. This method has been substantiated by Chenicek and Whitman (2) who made a comparison of losses measured by careful gaging and parallel measurements on the apparatus suggested by Stauffer, Whitman, and Roberts.

As it was proposed to use the present apparatus for the same purpose, a series of tests was made to verify its applicability to this sort of measurement and to learn the accuracy with which losses could be determined.

In order to do this, losses of known magnitude were produced by weathering samples of several commercial grades of gasoline. The original and the weathered samples were run in the vapor pressure apparatus and the losses estimated from the vapor pressure-per cent evaporated curves. At the start of these tests the apparatus and a definite plan of procedure were turned over to an experienced operator who carried out the entire series of tests. No check runs were made and the loss data are those obtained as the result of a single carefully made test.

Figure 6 shows the known losses plotted against the values estimated from the vapor pressure measurements. The solid 45° line indicates the locus of points for perfect agreement between the known and experimentally determined evaporation losses. The black dots on either side of the line represent the experimental points and indicate their approach to perfect agreement with the known losses.

The points in Figure 7 show the actual per cent error of the estimated loss plotted against the known loss. The solid line gives the probable per cent error (based on the average deviation of the points in Figure 6, regardless of sign) that might be expected in measuring losses of various magnitudes by this method.

VAPOR-LOCKING CHARACTERISTICS OF GASOLINES. In recent publications on the subject of vapor lock (1, 5) it has been shown that a gasoline in the fuel system of a car will cause vapor lock if, at the existing fuel system temperature, it forms more vapor than the fuel system can handle without disturbing the flow of liquid gasoline enough to interrupt normal engine operation. The available data further indicate that many cars can handle relatively large quantities of vapor, from $V/L = 10$ to $V/L = 50$ and greater (where V/L is the volume of vapor divided by the volume of liquid, both measured at the existing temperature and pressure) being the range of values reported for current model cars.

To tie in with this conception of the problem, the vapor-locking characteristics of the gasoline are expressed by a curve showing the quantity of vapor formed plotted as a

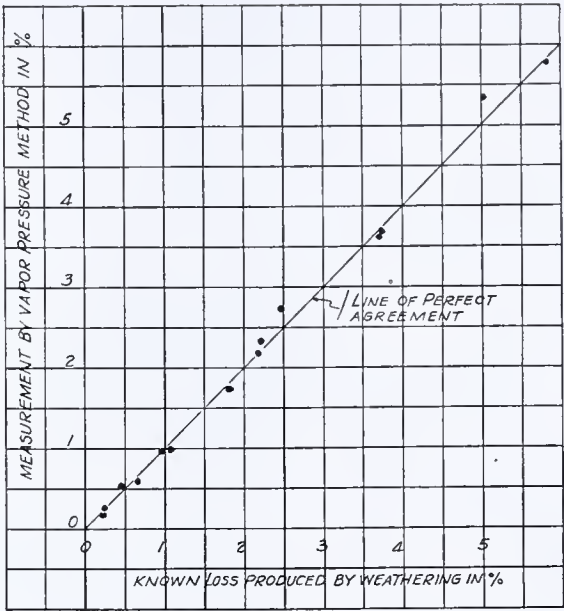


FIGURE 6. AGREEMENT BETWEEN KNOWN LOSSES AND MEASUREMENTS BY VAPOR PRESSURE METHOD

function of the boiling temperature, at the pressure existing in the fuel system. Bridgeman (1) has shown how such a curve can be established by running vapor pressure tests at various vapor-to-liquid volume ratios in a bomb similar to that used in the Reid vapor pressure test. In this method the vapor pressure measurements were converted to boiling temperature and plotted against vapor-to-liquid volume ratio.

The variable vapor-volume apparatus offers a very convenient means by which to obtain the same sort of information. Figure 8 gives the vapor-locking characteristics of six representative gasolines that have been evaluated in this manner.

The application of these data to corresponding data on car vapor-locking characteristics brings up an interesting point. Take, for example, the case of a popular 1934 model car having a vapor-handling capacity of $V/L = 34$ and fuel system temperature of 45° C. (113° F.) under certain operating conditions. When this car is operated under those conditions on a fuel having the vapor-locking characteristics shown

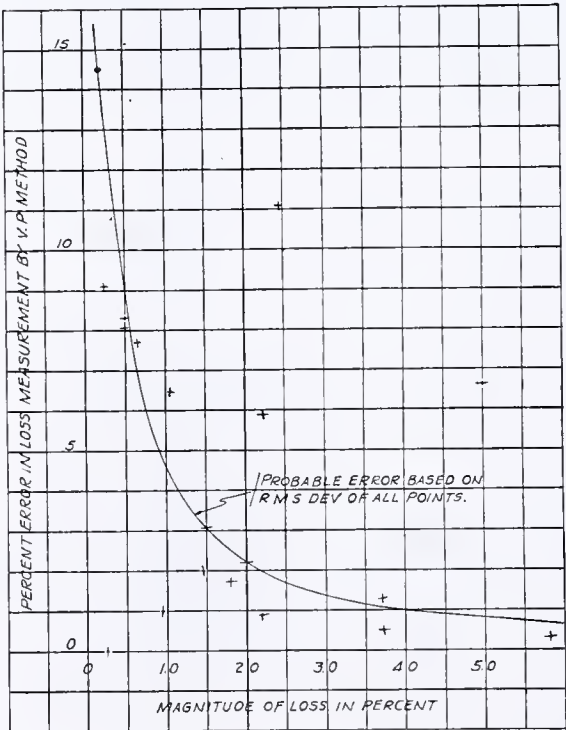


FIGURE 7. ERRORS IN LOSSES MEASURED BY VAPOR PRESSURE METHOD

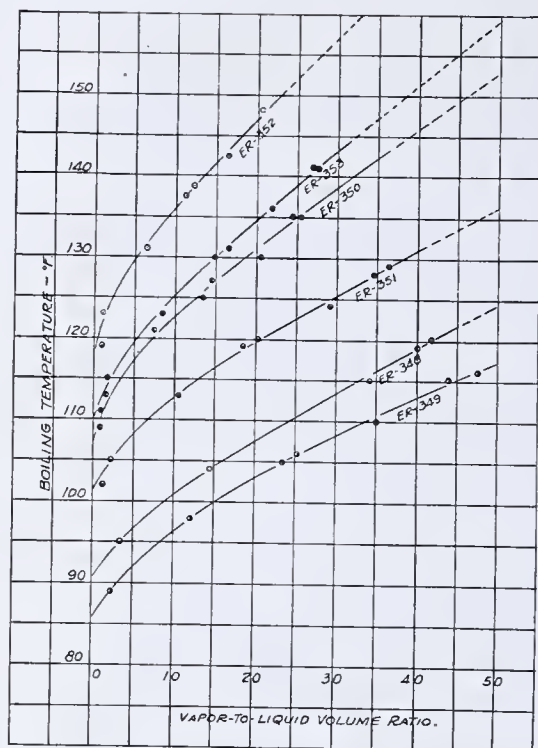


FIGURE 8. VAPOR LOCKING CHARACTERISTICS OF SIX REPRESENTATIVE GASOLINES DETERMINATIONS BY VAPOR PRESSURE METHOD

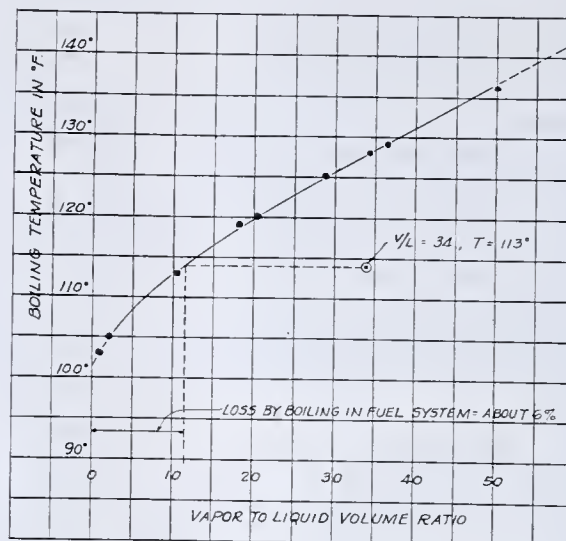


FIGURE 9. OCCURRENCE OF EVAPORATION LOSSES FROM FUEL SYSTEM OF A CAR IN WHICH VAPOR LOCK IS PREVENTED BY INCREASED VAPOR-HANDLING CAPACITY

in Figure 9, it is seen to be free from vapor lock because at 45° C. (113° F.) less than the limiting quantity of vapor will be formed. However, by projecting the point $V/L = 34$ and $T = 113^\circ$ F. horizontally to the curve for the gasoline characteristics, it is seen that a quantity of vapor equivalent to $V/L = 11.5$ is being formed in the fuel system, and since it cannot possibly get through the carburetor jet into the manifold, it must be vented out of the carburetor. This represents a loss in liquid fuel supplied to the engine, equivalent to the amount required to form the quantity of vapor that is vented off from the fuel system, in this case about 6 per cent.

That this sort of loss actually occurs in cars has been verified on several occasions when samples were bled from the carburetor bowls of cars while they were running, and the samples compared with the original gasoline supplied to the car. With current model cars operating under approximately normal conditions, losses of as great as 10.8 per cent have been detected and during warm weather losses of 0.5 to 5

per cent appear to be quite normal. In addition to the volume loss which tends to decrease the over-all fuel economy, an octane depreciation of 2 to 3 units and a general decrease in volatility also result from these losses.

Conclusions

The barometric type of vapor pressure apparatus having a variable vapor volume offers a rapid and accurate method by which to determine the initial vapor pressures of volatile materials. Data of the sort obtained on this apparatus are useful in estimating evaporation losses and in

measuring the vapor-locking characteristics of gasolines. There are also several other problems, such as the estimation of volatile impurities, for which the apparatus may be useful.

Acknowledgment

The writers take this opportunity to make acknowledgment to C. E. Cummings, B. Hegeman, and Neil MacCoull who gave suggestions and advice which were of great assistance in the final development of the apparatus and method.

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Laboratory-Scale Ebullition Tube

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AFTER research work requiring boiling point determinations, for which the method of Siwoloboff was found most suitable, an adaptation of the ebullition tube used in this method proved of value in securing steady boiling of the liquid in a small-scale fractional distillation.

The ebullition tube consists of a thin glass rod, long enough to be held upright by resting against the neck of the vessel in which it is used. To the lower end of the rod is sealed a short length (less than 1 cm.) of open tube, the diameter of which should be as large as is convenient, 1-cm. tubes proving generally useful. For rapid distillation several tubes may be used, while for best results a vacuum distillation requires two or more small-diameter tubes, giving several rapid streams of small bubbles.

This piece of apparatus has proved useful in minimizing bumping in liquids boiled in test tubes, and especially in vacuum distillations, replacing the capillary tube usually used. The capillary must be carefully made, is fragile, is often in need of adjustment, and possesses the further disadvantage of passing air through the hot liquid.

After boiling and cooling, the liquid retreats into the open tube, finally filling it. On heating again, the liquid is likely to become superheated until the tube suddenly resumes normal operation with a bad bump. This may be avoided by lifting, draining, and replacing the tube before the second boiling.

RECEIVED August 31, 1936.

An Adjustable Sensitive Thermoregulator

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THERE are a number of sensitive thermoregulators described in the literature (1, 2, 3, 7) that can maintain thermostats constant to $\pm 0.001^\circ \text{C.}$ for long periods of time without much attention. Most of these regulators are either glass tubes filled with toluene and mercury or metal tubes filled with mercury. Every time the temperature of the bath is changed over a wide range it necessitates addition or removal of mercury in the regulator. In order to eliminate these operations, Parks (6) employed a tight-fitting rubber plunger in a side arm of the regulator. By raising or lowering this plunger, the temperature of the thermostat could be varied to within $\pm 0.02^\circ \text{C.}$ of the desired temperature.

The thermoregulator herein described is made of glass, filled with mercury. The adjustment mechanism is similar to that of Parks, but of permanent construction. With this regulator, the temperature of a 36-liter thermostat can be easily changed and maintained at 25° , 30° , 35° , and $40^\circ \pm 0.001^\circ \text{C.}$ For shorter periods (2 or 3 hours) sometimes no movements can be detected in the Beckmann thermometer.

This thermoregulator, shown in Figure 1, is made of thin-walled (0.8-mm.) Pyrex tubing, A (35-mm. outside diameter), with a number of large indentations, B, which are about 25 mm. wide at the opening and 25 mm. deep. The thickness of the walls of these indentations is only about 0.2 to 0.3 mm. This accounts

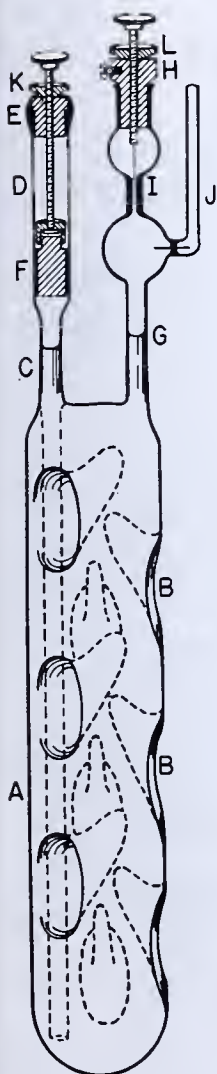


FIGURE 1

for the rapid response of this regulator to temperature changes in the bath. Extending inwardly in tube A, these indentations do not make the apparatus more fragile. To keep air from being trapped underneath these indentations when the regulator is being filled, they are pointed slightly upwards.

The adjustment mechanism, directly sealed to tube C that extends almost to the bottom of tube A, consists of a piece of Jena KPG tubing (5.05-mm. bore, 50 mm. in length) with a very uniform inside diameter (± 0.001 mm.). Attached with Picein cement to the top of this Jena tubing is a brass cap, E, through which passes a finely threaded brass rod carrying an Invar steel plunger, F. The diameter of the plunger is only slightly smaller (about 0.015 mm.) than the inside bore of the tube, but can be moved freely therein without using any lubricant.

The top of tube G is fitted with another brass cap, H, through which passes a rod carrying a fine nichrome wire that makes contact with the mercury at point I, where the fine capillary tube (0.7-mm. bore) opens into the upper bulb. Side arm J is for the other electrical contact. K and L are lock nuts.

With the plunger removed, redistilled mercury is introduced into the regulator through a funnel with a fine capillary stem reaching to the bottom of tube C. The mercury rises very slowly in tube A, so that no air bubbles can be trapped therein. Care is taken to keep the stem of the funnel full during the filling operation; otherwise air is forced into the regulator. When the mercury reaches halfway up in tube D, the funnel is removed and the plunger carefully replaced. In so doing the mercury level in tube D is pushed downward while that in tube G rises. The pressure created by the difference in these mercury levels will soon completely force out all the air trapped between the mercury and the plunger. The plunger in tube D is not air-tight, although no mercury can escape, and therefore the bottom of the plunger should always be slightly below point I, so that there is a positive

pressure against the plunger, thus preventing air from entering.

The adjustment mechanism can be made to operate over a wide temperature range by varying either the bore or the length of the Jena KPG tube. The thermoregulator described here holds about 110 ml. of mercury and has a temperature range of 80°C. (20° to 100°C.).

As pointed out by Geer (3) and others, an accurately controlled thermostat requires more than just a sensitive thermoregulator. It depends just as much on the type of heater, the relay, the thermal insulation of the bath, the regulator suspension, and the stirring. The modified radio tube relay system (5) used requires less than 2 microamperes through the regulator, so that there is no sparking at the mercury contact.

Figure 2 shows a modified Heisig and Camerson (4) type of double-walled thermoregulator with indentations in the inner tube to increase the surface and reduce the wall thickness. This regulator has about the same sensitivity as the one shown in Figure 1, but requires less mercury (about 70 ml.). The inside and outside tubes being only about 3 mm. apart, it requires some glass-blowing skill to make the upper and lower ring seals, while an amateur glass blower can make one of the types shown in Figure 1 without difficulty.

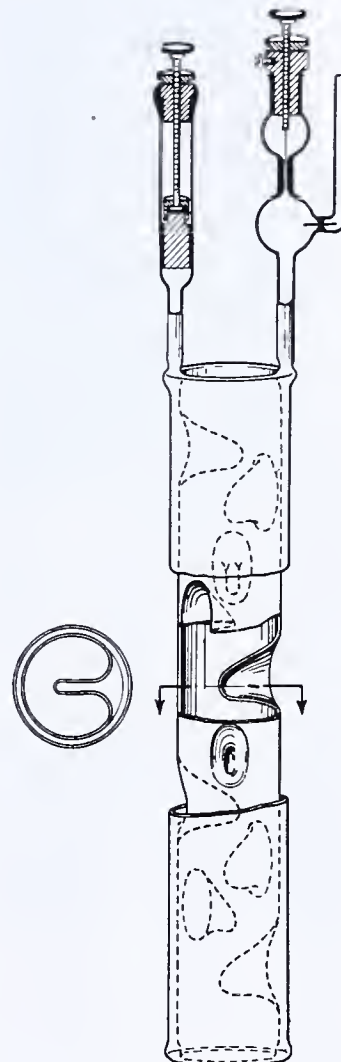


FIGURE 2

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- (1) Beaver, D. J., and J. J., *IND. ENG. CHEM.*, **15**, 359 (1923).
- (2) Ferguson, A. L., Van Leute, K., and Hitchens, R., *Ibid.*, *Anal. Ed.*, **4**, 218 (1932).
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- (4) Heisig, G. B., and Camerson, A. E., *IND. ENG. CHEM.*, *Anal. Ed.*, **5**, 420 (1933).
- (5) Heisig, G. B., and Gernes, D. C., *Ibid.*, **6**, 155 (1934).
- (6) Parks, W. G., *Ibid.*, **5**, 357 (1933).
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RECEIVED August 17, 1936.

CORRECTION. In the article entitled "Quantitative Separation and Determination of Aluminum and Zinc" [*IND. ENG. CHEM.*, *Anal. Ed.*, **8**, 349 (1936)] by F. H. Fish and J. M. Smith, Jr., no reference was made to the work published by H. A. Horan and J. B. Damiano [*J. Am. Chem. Soc.*, **57**, 2434 (1935)]. We sincerely regret the omission of this important reference.

Reference 2 at the end of the article should have read: Heyrovsky, J., *J. Chem. Soc.*, **117**, 1013 (1920).

F. H. FISH

Apparatus for the Fractional Distillation of Liquefied Gases

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LOW-temperature fractionating columns of numerous designs have been described by Frey and Yant (10), Oberfell and Alden (17), Podbielniak (20), Davis (2), Boschart (1), and others (3, 7, 9, 12, 13, 14, 18, 19, 21, 23). These columns are all characterized by a partial condenser, and fractionation takes place in a closed system. McMillan (16) has recently patented an improved form of such apparatus. In order to obtain a smooth boiling point curve, close and continuous attention must be given to the pressure inside the column and to the condenser temperature because of the effect of these factors on the boiling point observed. The successful operation of the columns requires considerable skill and experience, especially when the mixture being analyzed contains components boiling near one another. The apparatus described here is such that its operation can be easily mastered and it gives a boiling point curve that is smooth and independent of all reasonable variations in condenser temperature and heat input to the still. At the same time the apparatus is relatively inexpensive and simply constructed.

A packed glass fractionating column 310 mm. (12 inches) long and 6.3 mm. (0.25 inch) in inside diameter, fitted with a 25-cc. still and a condenser, is kept cold by placing it in a large Dewar tube 50 by 620 mm. (2 × 24 inches) in inside dimensions (Figure 1). The condenser of the column is cooled by passing liquid air or cold air through it. The cold air coming from the condenser is passed through the length of the Dewar tube and thus keeps

the entire apparatus in an environment suitable for operation. The packed section is surrounded by a closely fitting but not actually sealed outer jacket, which creates a dead air space and thus partially insulates the column from its environment. Since the column has no vacuum jacket, its construction involves only simple glass blowing. The large Dewar tube can be purchased complete at a cost only about three times that of a wide-mouthed quart-size Pyrex Dewar. Several different columns, each with certain special characteristics highly developed, can be inexpensively constructed and used with the same large Dewar tube and other accessory apparatus.

The column is designed for total condensation, the product being taken off as a gas through a side arm just below the condenser, while the top of the condenser may be left open to the atmosphere. Variations of pressure in the column and the resulting effects on boiling points are thus entirely eliminated, even though the condenser temperature may vary widely. The condenser is purposely constructed with a large heat capacity, so that its temperature cannot change suddenly or vary rapidly to any great extent. It follows that the apparatus may be operated with only slight fluctuations in pressure and boiling point, even when the top of the condenser is shut off entirely from the atmosphere, as in vacuum or pressure distillation, or in the preparation of a pure substance when it is desirable to be absolutely certain that no contamination occurs.

A simple semi-automatic device is used to control the rate at which liquid air is supplied to the condenser, so that the

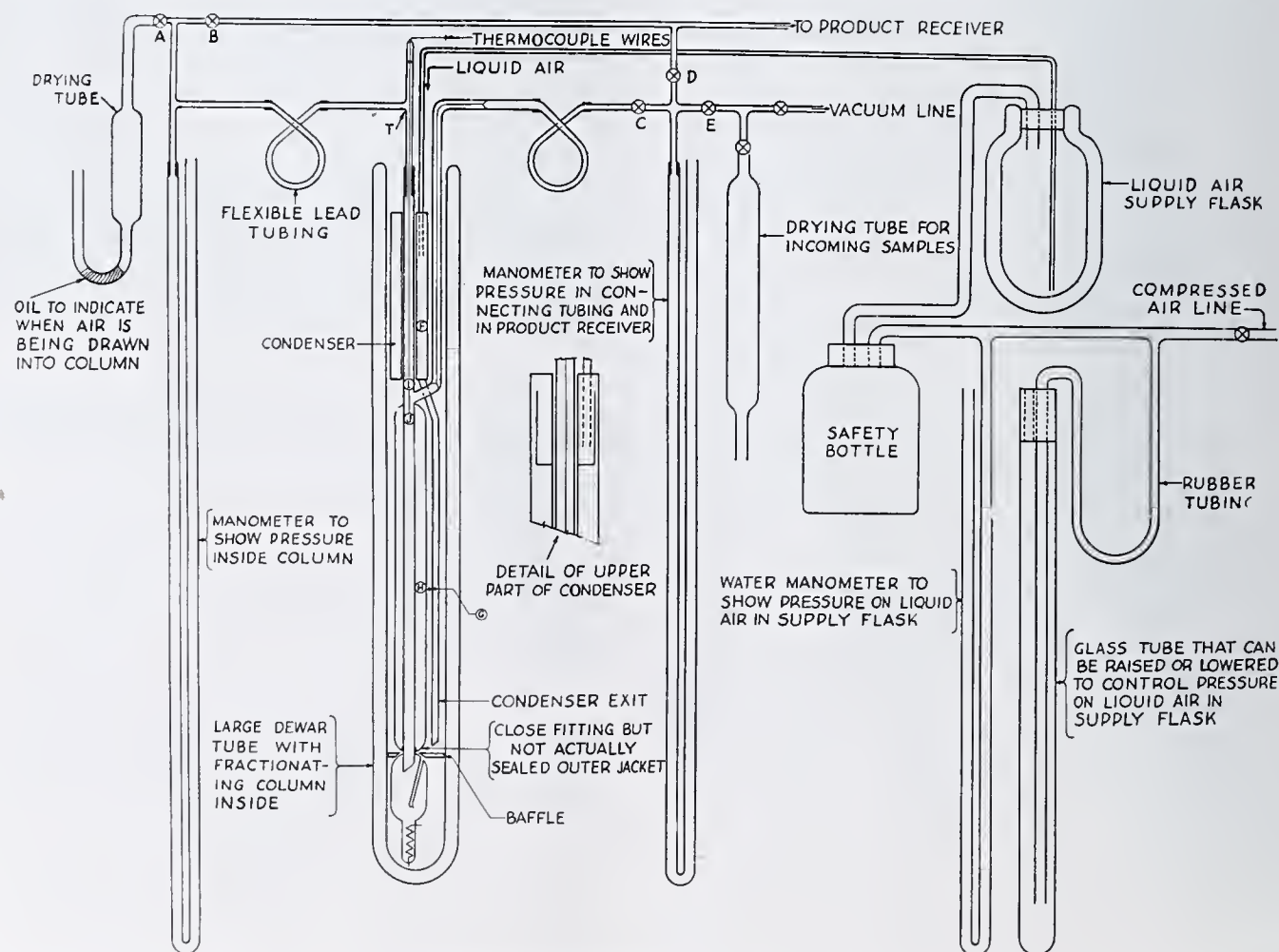


FIGURE 1. DIAGRAM OF APPARATUS

temperature of the latter is kept between narrow limits and need be observed and regulated only occasionally. The column has about ten theoretical plates, a holdup of 0.6 to 1.2 cc., and will not flood until about 1 cc. per minute of liquid is passing down the column and an equivalent amount of vapor is ascending. The product is usually taken off at rates of 5 to 25 cc. of gas per minute, but with certain mixtures rates of 75 to 100 cc. of gas per minute are possible without disturbing the equilibrium of the column. The liquid air requirement is about 0.5 liter per hour.

Details of Construction and Assembly

The large Dewar tube is entirely silvered except for two longitudinal strips 15 mm. wide on opposite sides which make it possible to observe the packed section and the still. The Dewar tube is enclosed in a box with glass front and back which is sealed and kept filled with dry air. This box protects the large Dewar from breakage and prevents condensation and frosting which would destroy visibility of the packed section. The still of the column is heated by a 100-watt internal heater of resistance wire sealed to copper wires carried through the glass with thin-walled platinum tubes. The packing may consist of small glass triangles (Figure 2) or single-turn glass (24) or wire (6) helices. The former was used in all experiments described here because experiments in this laboratory (8) indicated its superiority as to efficiency, holdup, and throughput.

To prevent condensation in the side arm of the column it is wound with a heater of resistance wire and this covered with a loosely fitting asbestos sleeve. The side arm is connected by flexible capillary lead tubing to the diaphragm valve, *C* (Figure 1), which in turn is connected to a manometer and through diaphragm valves *D* and *E* to the product receivers and to the vacuum line and inlet gas sample drier, respectively.

Connections to the top of the column are made through the glass *T* into the top of which thermocouple wires are first carefully sealed with de Khotinsky cement to make a gas-tight seal. After the condenser is in place enough packing is placed in the column to reach *J*. To keep the thermocouple junction centered in the column it is fitted with a wire spiral, the last turn of which is the same diameter as the inside of the column. All other turns of the spiral are of small diameter, just large enough to be slipped over the thermocouple wires to which it is tied with thread. The end of the thermocouple wire is then pushed into the top of the column about 2.5 cm. (1 inch) and more packing placed around it. Another spiral is then fastened in place to keep the packing from rising out of place. The thermocouple wire is then pushed down until its end touches the main body of packing at *J*. In order to get correct boiling point readings it is essential to have an inch of packing immediately above the end of the thermocouple wire and to have the wire centered in the column. When this is achieved the *T* is sealed to the top of the column with de Khotinsky cement. The side of the *T*-tube is connected to a manometer which measures the pressure in the column and also by means of flexible capillary lead tubing to the diaphragm valves, *A* and *B*, leading to the atmosphere and to the product receiver, respectively. Diaphragm valves are very advantageous because after they are once assembled and tested they can be depended upon to be gas-tight even under considerable pressure until the seat becomes worn. Stopcock grease troubles are also avoided. The diaphragm valves on the market at present, however, have more dead space than is desirable for the distillation of small samples.

Two thermocouples are located in the packing just below the side arm, *J*, and another about 2.5 cm. (1 inch) above the side arm, *I*. The former are used to measure the boiling point of the product being taken off, and the latter to make sure that the reflux coming from the condenser is not too cold. Thermocouples are also located inside and outside the air jacket, *G*, *H*, so that the temperature differential between the material in the column and the air in the large Dewar tube can be estimated and kept at a minimum. With this arrangement the environment of the column is maintained within a few degrees of the temperature of the column itself. All temperatures are measured with copper-constantan thermocouples and a high-resistance millivoltmeter which can be read to 0.01 millivolt (0.4° C.).

The condenser is made from two concentric pieces of thin-walled steel tubing of proper dimensions, to which ends and

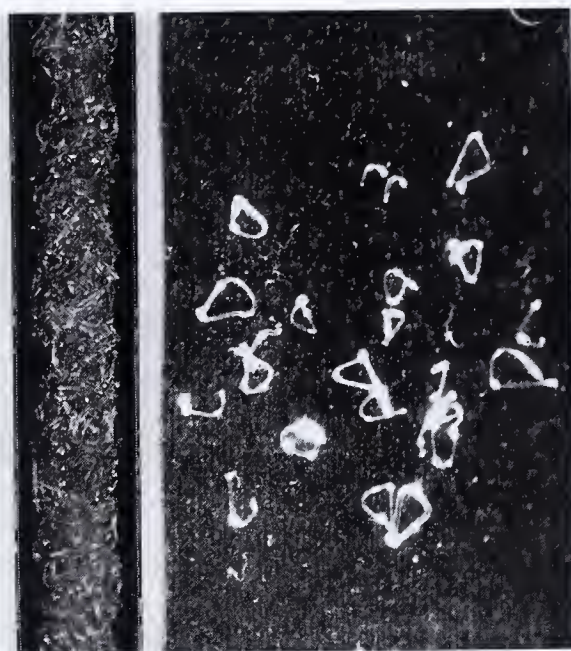


FIGURE 2. GLASS PACKING FOR COLUMN

Packed section of column, and individual pieces of irregular glass triangles used as packing

connecting tubes are brazed or soldered. The inner diameter of the inner tube of the condenser and the outer diameter of the glass part of the column over which it fits are made of such a size that there is very little clearance between them. Further to improve the heat transference across this small air gap, it is filled with a low-melting wax.

There is a baffle in the upper part of the condenser to prevent the incoming cold air (or liquid air) from passing directly to the lower end of the condenser. The condenser is packed with lead or copper shot to give it a relatively large heat capacity and to baffle the cold air further. The large heat capacity makes it very easy to keep the condenser near a desired temperature. Liquid air is supplied to the condenser directly from a 5- or 15-liter supply flask through a siphon which connects to the top of the condenser by means of as short a section of connecting tubing as possible. That part of the siphon that extends into the liquid-air supply flask should be of glass or other material of low heat conductivity to avoid undue consumption of liquid air. The slow current of cold air issuing from the mouth of the large Dewar tube causes formation of some frost. This frost is prevented from dropping back into the Dewar tube by packing the topmost 5 cm. (2 inches) of the tube loosely with cloth. At the end of a distillation the frost should be blown away with a stream of air, and the cloth removed and dried. To prevent frost and liquid water from condensing inside the Dewar tube after a distillation, a slow stream of dry air should be passed through the condenser until it warms up to room temperature. The use of small liquid-air supply flasks is subject to the disadvantage that occasional sudden ebullition (bumping) of the liquid air greatly increases its rate of transfer to the condenser and thus the temperature of the latter is caused to vary. In small liquid-air supply flasks the level of the liquid air drops rather rapidly and frequent adjustment of the air pressure forcing liquid air into the condenser is required to maintain condenser temperature constant.

Control of Condenser Temperature

The rate at which liquid air is supplied to the condenser and thus the temperature of the condenser is controlled (Figure 1) by maintaining a suitable air pressure (equivalent to 30 to 60 cm., 12 to 24 inches, of water) above the liquid air in the supply flask. This is best done by connecting to a compressed-air line through a needle valve and allowing excess air to bubble out through a tube, containing a suitable height of water which can be easily varied. By providing the column manometer with an extra arm (not shown in diagram) leading to the bottom of the tube through which the excess air is bubbling, the temperature control of the column can be made nearly automatic.

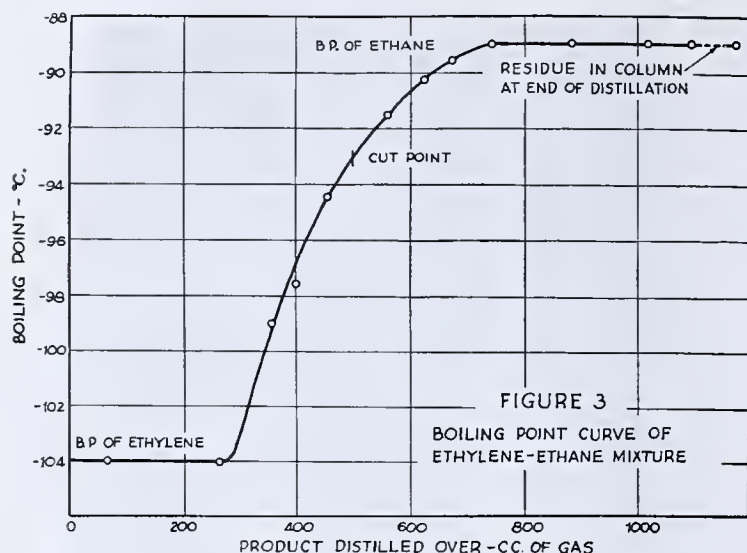


FIGURE 3. BOILING POINT CURVE OF ETHYLENE-ETHANE MIXTURE

Synthetic mixture containing 57.5 per cent ethane and 42.5 per cent ethylene. Total volume of sample was 1185 cc. of gas, equivalent to approximately 3 cc. of liquid. True volume of ethylene was 505 cc., while that found from this analysis was 500 cc. Time required for analysis was 2 hours. Reflux ratio was 15 to 1. Rate of take-off was approximately 10 cc. of gas (at 20° C.) per minute, rate of boiling 10 drops per minute, equivalent to 0.5 cc. of liquid or 100 cc. of gas (at -100° C.) per minute. Air outside air jacket was approximately 5° colder than air inside air jacket.

Operation of the Column

The sample is allowed to enter the previously evacuated column through its side arm by way of the inlet sample drier and valves *E* and *C* (*A*, *B*, and *D* being closed) until a pressure of about one atmosphere is reached. Liquid air is forced into the condenser rapidly until it reaches a temperature about 60° C. below the boiling point of the lowest boiling condensable gas in the sample, as measured by thermometer at *F*. The pressure on the liquid air in the supply flask is then adjusted so that approximately this temperature is maintained. As the sample condenses in the condenser and runs into the still, more sample is allowed to enter. This process can be hurried in the case of lower boiling gases (ethylene, methane, etc.) by placing a small amount of liquid air in the bottom of the large Dewar tube. In case there are in the sample appreciable amounts of gases not condensable by liquid air, the accumulation of these will cause the pressure in the column to rise. When enough of such gases have accumulated to give a pressure greater than atmospheric, they are slowly removed through valve *B* into the product receiver and then examined further by conventional means in order to determine their composition.

When all the condensable portion of the sample is in the column, valves *B* and *C* are closed and the heat input to the still is adjusted until the desired rate of boiling is reached. If it is desired to distill methane, it is necessary to keep the condenser so cold that drops of liquid air occasionally fall from the condenser exit. Under such conditions there is no difficulty in refluxing methane. If the pressure in the column rises to greater than atmospheric, the noncondensable gases causing this are removed as before. If the pressure becomes constant at some value below atmospheric, air is allowed to enter slowly through valve *A* until the desired pressure is attained. If the distillation is to be carried out at atmospheric pressure, valve *A* may be left open. The liquid-air supply to the condenser should be adjusted so that the temperature of air in the large Dewar is within 15° of the boiling point of the product being taken off. This is most easily done by noting the condenser temperature corresponding to the correct liquid-air supply and then maintaining the condenser at this temperature.

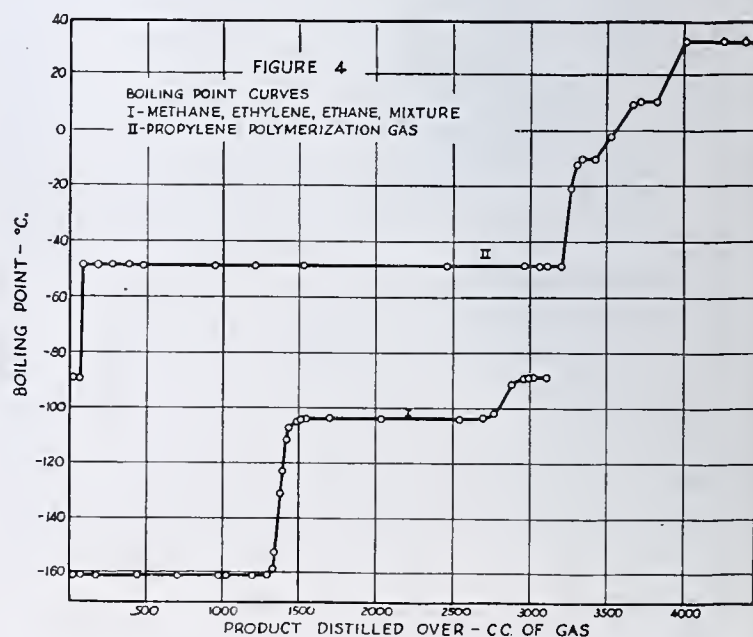
From this point on the operation of the column is very similar to that of an ordinary packed column, the product being taken off through valves *C* and *D* into the product receiver. The usual readings of boiling point and amount of product taken off are made and recorded at suitable intervals. The rate of take-off (along a plateau of the boiling point curve) may be 75 to 100 cc. of gas per minute without disturbing the equilibrium in the column, but rates of 5 to 25 cc. per minute are generally more satisfactory. When the tem-

perature at the top of the packing shows signs of increasing, the rate of take-off may be decreased to give a higher reflux ratio. If desired, the column may be allowed to operate under total reflux for a suitable period. As the temperature of the top of the packing rises and approaches the boiling point of the next component, the temperature of the condenser may also be allowed to rise to about the same extent. The size of the intermediate fraction between two pure substances can be decreased if 25 to 75 cc. of product are removed through the top of the column after the boiling point is about midway between those of the two pure substances. This results in the removal of any of the lower-boiling component that may be trapped in the condenser.

If the column floods at any time the trouble is either too much heat input to the still, or too high a temperature in the large Dewar, so that reboiling is taking place in the packed section. In the latter case the remedy is to supply a little more liquid air to the condenser, thus lowering the temperature of the entire apparatus. If there is a tendency to draw in air through the condenser, or if the pressure in the column drops when the product is taken off, the rate of boiling is too low and heat input to the pot should be increased, or the temperature of the air in the large Dewar is too low and should be allowed to rise by decreasing liquid air supplied to the condenser.

Typical Results Obtained with the Column

Mixtures of ethane (boiling point -89° C.) and ethylene (boiling point -104° C.) were chosen to illustrate the results that can be obtained with the column (Figure 3). The boiling points of these two hydrocarbons are close enough to one another ($\alpha = 2.25$) so that a real test of the apparatus is afforded, and they are also near the middle of the temperature range for which the column is intended. Results of other distillations are also shown (Figure 4). In examining these boiling point curves it is to be emphasized that the same smooth curve would be obtained even if the readings were taken and recorded by automatic devices so as to give a continuous series of points. Experiments with ethylene-ethane mixtures of known composition have shown that the distillation curves can be used to calculate the volume of either component in such a mixture to within ± 40 cc. of its true volume, if a minimum of 400 cc. of that component is present. If the vapor pressure ratio of the components being separated is more favorable, the results will be correspondingly improved. The equal volume method of determining the cut point was used. The equivalent of about 150 cc. of gas remains in the



column at the end of a distillation after reflux stops. Figure 5 shows the results of a distillation in which condenser temperature, heat input to pot, rate of boiling, and rate of take-off were purposely varied over a considerable range. The observed boiling point varied only slightly.

The correct determination of the boiling point of the material at the top of a small fractionating column is a difficult matter. The total mass and therefore the total heat capacity of the material around the thermocouple junction are quite small and so even a small gain or loss of heat from the surroundings destroys the vapor-liquid equilibrium. There is need for the development of some different method for determining the composition of the material at the top of a small fractionating column. The method should preferably give continuous readings on very small amounts of material, and be such that extended empirical calibrations are not required. Viscosity, thermal conductivity, refractive index, and optical and electrical properties have not yet been thoroughly investigated.

Distilling Capacity, Efficiency, and Holdup

The maximum distilling capacity was estimated from the number of drops per minute falling back into the pot. This was done with both benzene-carbon tetrachloride and low-boiling hydrocarbon mixtures and the results ranged around 1 cc. of liquid per minute.

The efficiency was determined with a mixture of benzene and carbon tetrachloride after the column had been slightly modified so that samples could be removed from the pot. In a typical experiment the refractive index of the pot sample was $n_D^{20} = 1.4901$, while that of the side arm was 1.4779. In another experiment the corresponding figures were 1.4889 and 1.4782. Reference to the vapor-liquid equilibrium diagram for benzene-carbon tetrachloride indicates approximately ten theoretical plates (5, 15).

An attempt was also made to determine the number of theoretical plates with a mixture of ethane and ethylene. After equilibrium had been reached with a mixture of ethane and ethylene in the column, small samples were removed and analyzed by absorption with fuming sulfuric acid. In a typical experiment the vapors from the pot analyzed 7.7 per cent ethylene, while the side-arm sample analyzed 88.0 per cent ethylene. This gives a value of approximately 88.0 for the enrichment ratio. The vapor-liquid equilibrium relations of ethane-ethylene mixtures are not known, and since the meager evidence (11) available indicates that Raoult's law may not hold true for the above system, the equivalent number of theoretical plates was not calculated (4).

The holdup was estimated by collecting separately as a gas the ethane in the column at the end of a distillation when the pot was just dry. The holdup naturally varied with the vapor velocity and ranged from 0.6 to 1.2 cc. of liquid.

It is to be emphasized that a decrease in holdup by itself cannot be equivalent to an increase in equivalent number of theoretical plates. Some confusion has probably resulted because it has not been recognized that as the rate of boiling and therefore the liquid holdup in a column are decreased the number of theoretical plates may actually increase markedly (22). Often the improved fractionation is accredited entirely to the decreased holdup, while actually it is due in a large measure to increased number of plates.

It is not low holdup alone, but low holdup per plate that is desirable. The disadvantage of large holdup can often be overcome by increasing the size of the sample being distilled, but a column with a small number of theoretical plates will be satisfactory only for separations in which the vapor pressure ratio is large (C_2 from C_3 , or C_3 from C_4 hydrocarbons). Serious difficulties are encountered when the ratio is small and boiling points are close together (isobutane from iso-

butene, butene-1 from *n*-butane, etc.). These difficulties will persist regardless of any changes in holdup or other characteristics, unless the equivalent number of theoretical plates is increased. This is illustrated by the figures in Table I. In part A of Table I it has been assumed that fractionation of a butene-1-*n*-butane mixture has reached the equilibrium stage when the molal ratio of these components in the still is unity. The per cent composition is given in the first column of the table. The second column gives the vapor pressure ratio for the mixture being distilled. The fourth and fifth columns give, respectively, the enrichment factors and the percentage compositions of products at the top of the column for columns of different numbers of theoretical plates as indicated in the third column. Parts B, C, D, and E of Table I give corresponding data for other commonly encountered mixtures. These relationships will hold regardless of any changes in holdup in the column since the conditions are those of total reflux. It has been recognized that the separation of mixtures like D and E is much easier than the separation of those like A and B. Table I gives a quantitative measure of this difference, and relates it to the equivalent number of theoretical plates in a column. Table II gives the vapor pressure ratios for other common mixtures.

TABLE I. EFFECT OF EQUIVALENT NUMBER OF THEORETICAL PLATES

Composition of Liquid in Still	Vapor Pressure Ratio	Number of Plates in Column	Enrichment Factor	Composition of Product	
				Butene-1 %	<i>n</i> -Butane %
A 50% butene-1 50% <i>n</i> -butane	1.2	1	1.2	54.5	45.5
		2	1.44	59	41
		5	2.5	71	29
		10	6.2	86	14
		20	39	97.6	2.4
		30	240	99.4	0.6
B 50% isobutane 50% <i>n</i> -butane	1.6	1	1.6	Isobutane 61.5	<i>n</i> -Butane 38.5
		2	2.56	72	28
		5	10.5	91	9
		10	101	99	1
		20	12,000	100	0
		30	1,300,000	100	0
C 50% propane 50% isobutane	3.5	1	3.5	Propane 78	Isobutane 22
		2	12.2	92.3	8
		5	520	99.7	3
		10	6350	99.95	0.05
		20	400,000	100	0
		30		
D 50% ethane 50% propane	10	1	10	Ethane 90	Propane 10
		2	100	99	1
		5	10,000	99.99	0.01
		10	10,000,000		
		20		
		30		
E 50% ethane 50% methane	50	1	50	Methane 98	Ethane 2
		2	2500	99.96	0.04

TABLE II. VAPOR PRESSURE RATIO FOR HYDROCARBON PAIRS

Components	At B. P. of More Volatile Component	At B. P. of Less Volatile Component
Methane-ethane	505	37.7
Ethane-propane	15.2	6.8
Propane-isobutane	3.8	3.1
Isobutane- <i>n</i> -butane	1.58	1.55
<i>n</i> -Butane-isopentane	3.04	2.72
Isopentane-pentane	1.38	1.36
Methane-ethylene	200	23
Ethylene-ethane	2.45	2.27
Ethane-propylene	10	6.5
Propylene-propane	...	1.25
Isobutane-isobutene	1.22	1.21
Isobutene-butene-1	1.02	...
Butene-1- <i>n</i> -butane	1.21	1.20
<i>n</i> -Butane- <i>cis</i> -butene-2	1.05	...
<i>cis</i> -Butene-2- <i>trans</i> -butene-2	1.11	1.10

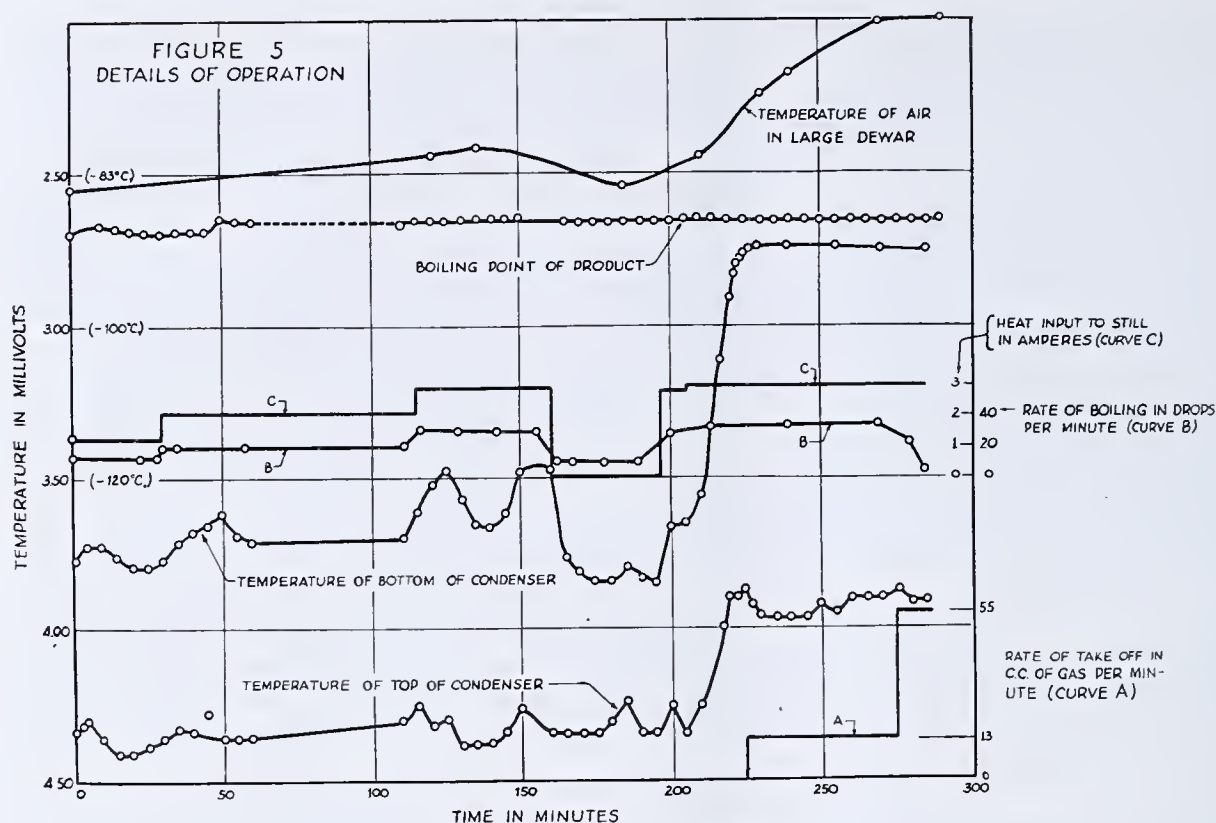


FIGURE 5. DETAILS OF OPERATION

Shows smooth nature of boiling point curve, even when there are large variations in condenser temperature, heat input to pot, and rate of take-off. Top of column was open to atmosphere during this experiment, so there was no variation in pressure. During interval from 60 to 110 minutes on time scale, apparatus operated without any attention whatever.

The uncertainties in these calculations, due to lack of complete knowledge of vapor pressure and vapor-liquid equilibrium relations, are not great enough to have any marked effect on the results.

Limitations and Errors

It is not intended to represent that the apparatus makes sharper separations and requires smaller samples or less time for analysis than others that have been described. Its utility depends upon its ease and simplicity of operation, flexibility, relatively simple construction, and low cost, and upon the fact that it gives a correct boiling point curve even in separations where the vapor pressure ratio is unfavorable.

Certain errors are unavoidable in any distillation analysis. With the apparatus described here these are as follows:

1. At the beginning of a distillation some of the lowest boiling component is required to fill the dead space in and above the condenser, the line to the column manometer, and the side arm.
2. A further portion of the lowest boiling component is required to fill dead space between the diaphragm valve, *C*, and the product receiver.
3. The use of the equal volume method of determining the cut point may lead to error because the first half of the intermediate fraction may not contain half of each component.
4. At the end of a distillation, some of the highest boiling component remains in the column.

Errors 1 and 2 affect the analysis in two ways—i. e., they decrease the percentage of lowest boiling component below its true value and they decrease the total volume of the sample below its true value and therefore cause an increase in the percentage of all components. Error 3 affects the volume and percentage of each component present in a different way, since the magnitude of the error depends upon the nature of the vapor pressure-composition curve of the pair of components being separated. This error enters twice for each component except highest and lowest boiling components. Error 4 decreases the percentage of highest boiling component below its true value and decreases the total volume of the sample below its true value. It also necessitates the assumption

that all of the residue is the same composition as the last portion on which a boiling point could be obtained. Errors 1, 2, and 4 are easily corrected for by measuring the volume of the various parts of the column.

Several methods have been proposed for determining the exact volume of a given component from the distillation curve, including the equal volume, the equal area (20), and the equal mole fraction of vapor methods (7). Only the latter takes into account the fact that the first half of the intermediate fraction contains more than half of the lighter component. With the apparatus described here the equal volume method seems to give values as nearly correct as the precision of the results

warrants and this method has been used in the cases discussed here. In such calculations, it is not necessary to have an extremely sharp break in the distillation curve if the boiling points used in plotting the curve are the correct ones. The determination of the boiling points by means of a thermocouple in the packing below the side arm rather than in the condenser gives correct boiling points, since this causes the temperature of the thermocouple to be determined solely by the equilibrium mixture of liquid and vapor passing over it, and not by the temperature of the condenser.

Modifications

The apparatus is described here in its simplest and most generally useful form. Modifications of many kinds may be made to suit the requirements of particular types of distillation. The air jacket may be replaced by a strip-silvered vacuum jacket and the operation of the column then becomes even easier and efficiency will increase, but the cost of construction is increased. The use of this vacuum jacket is recommended in cases where the column is to be used by entirely inexperienced operators without supervision. The column may be operated as a partial condenser type, all products being taken off through the top of the column. If it is necessary to transfer samples to the still as liquid phase, a suitable connection of capillary tubing may be made directly to the bottom of the column.

Distillation of Complex Butane-Butene Mixtures

The problem of the analysis of mixtures containing isobutane (b. p. $-11^{\circ}\text{C}.$), isobutene (b. p. $-7^{\circ}\text{C}.$), butene-1 (b. p. $-6.5^{\circ}\text{C}.$), normal butane (b. p. $-0.5^{\circ}\text{C}.$), *cis*-butene-2 (b. p. $+1^{\circ}\text{C}.$), and *trans*-butene-2 (b. p. $+3.7^{\circ}\text{C}.$) has not yet been satisfactorily solved and will continue to be of importance because of the availability and reactivity of these substances. A successful analysis of such mixtures depends upon efficient fractionation with cuts between isobutane and isobutene, and between butene-1 and *n*-butane. Acid absorp-

tion or some physical property can then be used for analysis of the fractions, if the cuts are sufficiently sharp. Since the vapor pressure ratio for isobutane-isobutene or butene-1-*n*-butane is approximately 1.2, it is obvious that columns having on the order of ten theoretical plates will not be satisfactory since the enrichment factor is less than 7. However, a column like that described in this paper, but with a packed section about 90 cm. (3 feet) long, would have 30 or more plates and an enrichment factor of about 240. This would give the required sharpness and smooth operation, along with a reasonable throughput.

Experience with the column described above and other experiments on fractionation in small-diameter columns (22) suggest that at least some previously described columns, such as those referred to in the first paragraph of this paper, can be considerably improved for purposes of butane-butene distillation by modifying them as follows:

1. Use single-turn glass or wire helices as packing.
2. Relocate the thermocouple junction about 2.5 cm. (1 inch) below the bottom of the condenser.
3. Increase the heat capacity of the condenser by packing it with lead or copper shot.
4. Supply liquid air to the condenser at a constant rate by a device such as that described above.
5. Supplement the manually controlled take-off valve by an automatic sintered-glass mercury valve (16).

The combined effect of these modifications will be to increase the total time required, but the equivalent number of theoretical plates will be increased at practical rates of throughput, and irregular variations in the boiling point will be minimized because the direct transfer of heat from the thermocouple junction and its immediate surroundings is made more regular, pressure variations in the column are de-

creased, and efficiency of fractionation is stabilized at a high level.

Acknowledgment

The author wishes to acknowledge the suggestions and advice of M. R. Fenske and G. H. Fleming in the development of this apparatus.

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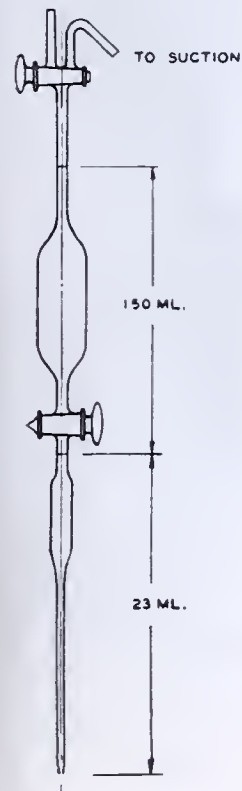
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Oil Acidity Pipet

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THE author's inspection and salvaging of transformer oil often required acidity determinations of many samples. The normal procedure included the weighing of a 20-gram sample, the addition of 150 ml. of benzene-methyl alcohol solvent, and titration with standard alcoholic potassium hydroxide, using alkali blue as an indicator. Evans and Davenport (1) showed this method to be superior to the contemporary tentative A. S. T. M. procedures. The apparatus described below, however, may be adapted for use in the current tentative A. S. T. M. Designation D188-27T by making it with the proper capacities for oil and solvent.

When there was a large number of samples the weighing seemed tedious and time-consuming. An investigation of the specific gravities of a considerable number of used transformer oils revealed slight differences, and suggested a simpler means of measuring the desired amount for analysis. At

25° C. the average weight of 23 ml. of samples from 20 different transformers was 20.041 grams. The maximum deviation from the mean was 0.133 gram. Since the probable error involved in measuring the sample by volume was considerably less than the error in titration, there could be no advantage in using the more precise weight method. A convenient way of measuring both the sample and solvent may be accomplished with the combination pipet shown in the diagram.

The particular feature of this apparatus is its self-rinsing property. The oil sample is drawn into the lower pipet and the oil adhering to the outer side of the tip may be wiped off before introducing the solvent, which is drawn in until the upper pipet is filled. The oil does not mix spontaneously with the solvent, but remains in the lower part of each pipet. When the contents are drained into the titration flask, the oil is washed completely from the pipet by the supernatant solvent. The apparatus may be used subsequently without further cleansing, and contamination is negligible.

The use of the special pipet in conjunction with a standard self-filling buret has reduced the time required for acidity determinations to 25 per cent of that required by the old procedure.

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RECEIVED August 29, 1936.

An Improved Design of Rodgers Ring Burner

G. FREDERICK SMITH, University of Illinois, Urbana, Ill.

THE Rodgers ring burner (E. H. Sargent Co., Catalog No. 2372) has so many features which may be used to advantage by the analytical chemist that additional attention ought to be directed to it by describing modifications in design which will extend its field of usefulness. Improvements which have been found by extended use to be very satisfactory are therefore described.

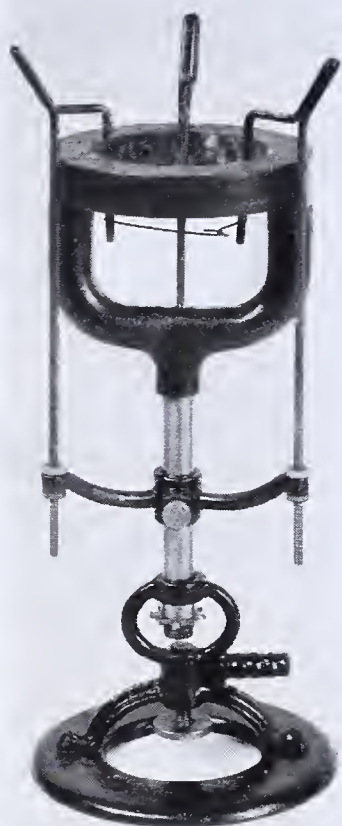


FIGURE 1. UNMODIFIED RODGERS BURNER

The unmodified Rodgers burner is shown in Figure 1. The design of base and gas and air adjustment are a cross between the P. G. and E. type of burner (A. H. Thomas Co., Catalog No. 2594) and the Boyce adjustable burner (Central Scientific Co., Catalog No. 11065). The gas intake is adjusted by a needle valve with milled-head disk which moves up and down at the lower end of the vertical tube, serving as mixing chamber as in the Boyce burner, with a bushing type of air-intake adjustment for altering proportions of gas and air burned as in the P. G. and E. type. The Rodgers burner terminates at the upper extremity in a bronze ring, 87 mm. outside diameter and 72 mm. inside diameter and 14 mm. thick, attached to the burner barrel by a hollow U-shaped support 40 mm. deep. There are 12 flame jet openings on the inside of the bronze ring approximately 3 mm. in diameter.

Supported by the gas-mixing tube of the Rodgers burner there is attached an inverted tripod support for three heavy-gage wires, terminating above the ring burner and returning inside the ring

to serve as supports for a triangle of nichrome wire threaded through holes drilled through the wire ends as shown in Figure 1.

The modified Rodgers ring burner is shown in Figure 2. The base of the apparatus has been greatly increased in diameter. An iron plate 3 mm. thick is cut 20 cm. in diameter, with the outside edge beveled and with an 80-mm. hole in the center. The base of the unmodified burner is attached to the new base with three screws, as shown in Figure 2. A calibrated aluminum disk is attached, using small screws, to the under side of the needle-valve regulator of the unmodified burner and a pointer is fastened to the regular base, as shown in section A-A. The barrel of the burner is calibrated to aid in adjusting the height of the wire crucible support on the burner barrel. The iron-wire crucible supports of the unmodified burner are removed and in their place a 4-mm. nichrome wire bent as shown is substituted. The triangular nichrome-wire crucible support of the original burner is replaced by a platinum wire.

A piece of stainless steel 45 mm. in diameter and 41 mm. high is drilled and machined to allow the insertion of a 25 to 35-ml. platinum crucible with a fairly close fit, as shown in Figure 3. The crucible should be left to protrude at the top 3 to 4 mm. This stainless-steel radiator just fits within the nichrome-wire crucible supports with their platinum-wire triangular base.

In use the burner is connected to the gas supply (natural or artificial gas), with the needle valve closed and the supply line valve open. The flame jet magnitude is then controlled by opening the calibrated needle-valve adjustment to the desired position and properly regulating the air mixture employed. A nichrome-wire gauze may be placed over the burner on the upright nichrome supports. A beaker placed over a flame on the wire gauze may be raised or lowered, using the adjusting screw on the calibrated burner barrel. Almost any degree of temperature ordinarily employed may be thus maintained to a very close margin, $\pm 5^\circ$ or even less. A wash bottle may be kept hot to the desired degree without boiling. A platinum crucible may be heated from the top downwards by supporting it on the platinum triangle and raising it

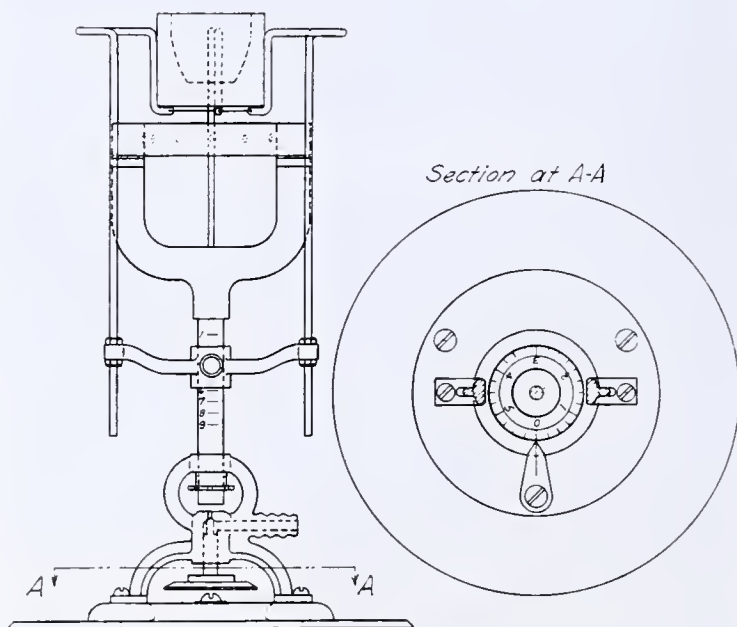


FIGURE 2. MODIFIED RODGERS RING BURNER
With stainless steel crucible radiator



FIGURE 3. MODIFIED RODGERS BURNER WITH
CRUCIBLE RADIATOR AND PLATINUM CRUCIBLE

gradually into the surrounding jets of the gas ring burner. The stainless-steel radiator may be inserted as shown in Figure 2 with an even better effect in the volatilization of sulfuric acid from a platinum crucible inserted within the radiator, or in the charring of filter paper prior to final ignition at low heat, and finally at higher heat, with the radiator removed. Many

other applications will occur to the analyst. The enlarged base provides needed stability not given by the unmodified Rodgers burner. The writer believes that the user of the newly formed burner will be well compensated for the effort involved in remodeling.

RECEIVED August 25, 1936.

Standard Liquids for the Microscopic Determination of Refractive Index

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THE refractive index of a material is a definite physical constant which, when easily determined, is a valuable aid to the rapid identification of many substances. Identification by this method has the advantage of not requiring the consumption of the material under investigation.

Microscopic methods for the determination of refractive indices are especially useful and have long been used in the identification of minerals (4), and more recently in the identification of alkaloids and fibers (3). Of the microscopic methods available, the most generally applicable are those comparing the index of refraction of the material with a liquid of known index.

In the Becke line method, the crystal or particle is immersed in a liquid of known index of refraction on a microscopic slide and viewed through a microscope with an objective whose numerical aperture is about 0.50. On raising the tube of the microscope, a halo of light around the particle moves from the medium of lower to the medium of higher index of refraction. By substituting other liquids the index of the material is obtained within the limits of the liquids available.

In the oblique illumination method the particle is similarly compared with liquids of known index. In this case an objective of low aperture is substituted and light is made to pass obliquely through the drop, either by tilting the mirror to one side or by shading a part of the light source. The crystal is shaded on one side. When using a substage condenser in the system the crystal is shaded on the same side as the shadow in the field if it has a higher index of refraction than the surrounding medium, and on the opposite side if its index is lower (1, 2, 4, 5).

The Becke line method serves best with particles having faces nearly perpendicular to the stage of the microscope; the oblique illumination method for particles whose cross sections are more nearly lenticular. Either device is capable of detecting a refractive index difference of 0.002 to 0.003. However, such small differences are seldom required.

Since comparison with liquids of known refractive index is the essence of the determination, a series of liquids whose refractive indices vary by small and regular intervals is required. Chamot and Mason (1) suggest such a list (p. 385). However, such lists contain many natural oils whose indices often are found to be different from the published values, furthermore, the intervals are not regular, varying from 0 to 0.02 in the range of the most frequently used liquids.

Such difficulties can be overcome by making artificial mixtures of totally miscible pure liquid compounds, whose refractive indices are far apart but whose vapor pressures are nearly the same (for stability). Not many liquid pairs have this desirable combination of properties, but a search of the literature revealed the fairly common compounds listed in Table I.

From Table I it is evident that the range of refractive index between 1.6582 and 1.4234 can be covered by mixtures of α -bromonaphthalene and heptylic acid and the range between

1.4981 and 1.3841 (or between 1.4234 and 1.3841 if no overlapping with the other series is desired) by mixtures of mesitylene and ethyl propionate. Furthermore, *n*-butyl phthalate can be substituted for the more expensive heptylic acid above 1.4932.

Chemicals of technical grade were employed. An Abbé refractometer was used for the refractive index determinations. For each pair of liquids to be mixed a graph was made relating the percentage by volume of each component and the refractive index of the mixture and from this graph was read the ratio of the components required to give the desired refractive index. The mixtures were made from small burets and the index was checked with the refractometer. If the agreement was not within 0.001 it was easily adjusted by trial and error and checking.

TABLE I. REFRACTIVE INDEX AND VAPOR PRESSURE OF ORGANIC LIQUIDS

Compound	Vapor Pressure		Refractive Index at 20°
	° C.	Mm.	
α -Bromonaphthalene	110	3.5	1.6582
<i>n</i> -Butyl phthalate	110	3.8	1.4932
Heptylic acid	90	1.9	1.4234
Mesitylene	20	27.15	1.4981
Ethyl propionate	20	27.75	1.3841

By this means a set of liquids from $n = 1.655$ to $n = 1.385$ with intervals of 0.005 was prepared. The mixtures were kept in small glass-stoppered bottles. One year after preparation the liquids containing α -bromonaphthalene and butyl phthalate or heptylic acid had remained constant to within a refractive index of 0.002, even though they had been inadvertently exposed to sunlight for an indefinite period. Under ordinary usage, the liquids containing ethyl propionate and mesitylene remained constant within 0.005 for a period of 3 months.

Since the liquid mixtures described above cover the range of refractive index of a large number of minerals and of all the common textile fibers, they are especially useful in these fields. Identification of organic compounds, of course, is limited to those which do not dissolve in the liquids.

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Preparation of Laboratory Refractory Crucibles

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FOR studies at very high temperature special refractory crucibles are required. Above 1500°C . the refractory materials usually considered are alumina, zirconia, magnesia, beryllia, and thoria and certain silicate compounds of these, such as mullite and zircon. These materials are all nonplastic, so that under ordinary circumstances they are not adapted to the operations of hand molding or casting so successfully employed with plastic clay. For the nonplastic refractories, forming the crucibles under mechanical pressure

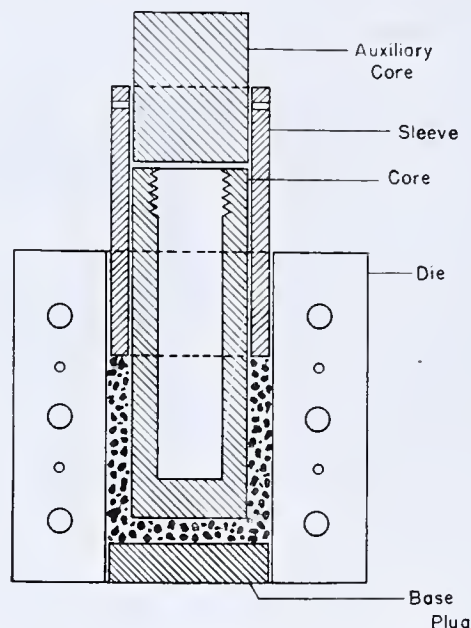


FIGURE 1. ASSEMBLY FOR FORMING CRUCIBLES

seems to be the most generally suitable. However, especially with thin-walled crucibles, considerable attention must be given to technic. A mode of operation has been described (1), the essential feature of which consists in securing an equal density after compression in the base and walls. The pressures required for this purpose are generally different for the walls and base. Equal density of compression results in a uniformly strong crucible, which can be made on a dependable production schedule.

The previous procedure consisted in forming the walls, leaving a very small ridge and welding the base to the walls at the ridge. Subsequent more extended work has shown that this two-stage procedure is not always successful, because of a relatively large discontinuity at the weld. A modified procedure was therefore developed which obtains the same results of equal density of compression without the variable discontinuity that exists in the two-stage method.

Modified Procedure

The assembled mold is shown in Figures 1 and 2. The core is hollowed out to reduce its weight. Operation is as follows:

With the steel die and base plug in place, sufficient damp powder is tamped in to provide the base. The core is then centered in position, and powder tamped in by means of the sleeve. With the help of the removable auxiliary core, pressure is successively applied to the walls and base in predetermined small steps until the final maximum pressure has been reached independently for both walls and base—usually different values. The relative pressure depends on the nature of and fineness of the material and on the amount of moistening agent. Its value is determined by density measurements on an oven-dried crucible.

After pressing, the mold is loosened and the sleeve is twisted in a

horizontal plane, so as to break the bond between it and the walls of the crucible. The core is similarly twisted by means of a bolt that screws into it, and is then lifted out with a rotary motion. If the sleeve does not come with the core it is lifted out separately.

By this procedure, even though the crucible wall be tamped in firmly, a gradient exists along the wall from the upper edge to the base. For example, for a zircon crucible, a load of 20 kg. on a 5-mm. wall 50 mm. long showed for the oven-dried product a density of 3.580 at the top third section and 3.319 at the bottom section, a difference of nearly 10 per cent. Corresponding to this difference in density, the top section of the green crucible was obviously much stronger than the bottom section.

Where it is desired to have a uniformly dense wall, the procedure may be altered by applying the final maximum pressure to the wall in three or more sections. To minimize the discontinuity thus incurred, the lower edge of the sleeve is made saw-toothed. Before applying pressure to each section of the wall, it is essential that the powder that has been tamped in be leveled by means of a rotary motion of the saw-toothed sleeve. Although the place where the sections meet is made visible by etching of the steel mold, no trouble during drying or firing has been experienced at that point. The topmost section of the wall is made with a smooth-edged sleeve.

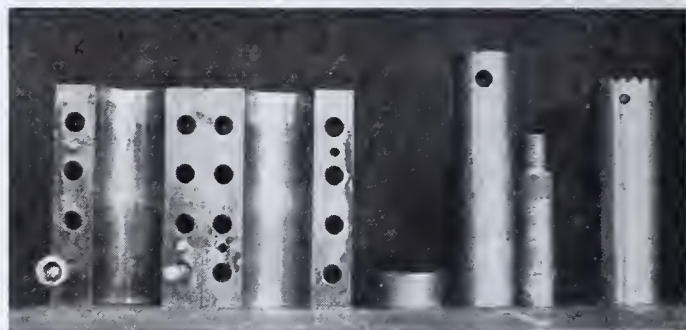


FIGURE 2. CRUCIBLE MOLD DISASSEMBLED

1. Die
2. Base plug
3. Core and auxiliary core
4. Sleeve

By means of the above procedures satisfactory large crucibles 5.0 cm. in diameter have been produced with a wall as thin as 3 mm. A thinner wall could probably also be had if desired.

The moistening solution consists solely of the slightly acid chloride of the refractory metal oxide. Small amounts of phosphate promote stability on firing (1). The green crucible may be placed in the drying oven within an hour after pressing. Firing is almost invariably to be done in an oxidizing atmosphere.

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RECEIVED August 6, 1936. Presented before the Division of Industrial and Engineering Chemistry at the 92nd Meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) This work was carried out at the Nonmetallic Minerals Experiment Station, U. S. Bureau of Mines, Rutgers University, New Brunswick, N. J.

Semi-Microdetermination of Acetyl

Especially in O-Acetyl Compounds

E. P. CLARK, Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture, Washington, D. C.

THE microdetermination of acetyl is a procedure in need of improvement, as evidenced by the numerous methods and their variants that have appeared during recent years (2). Except for special cases, these procedures may be grouped in two classes. The principle involved in the first class consists of aqueous acid hydrolysis followed by the distillation and estimation of the acetic acid formed; in the second class alcoholic acid hydrolysis is followed by the distillation of the resulting ethyl acetate along with the excess of alcohol, and finally the estimation of the acetyl in the ethyl acetate by hydrolysis with an excess of standard alkali.

The first type of these general methods is inapplicable to many classes of compounds, because aqueous acids will not affect hydrolysis. The second type of procedure is, in general, more reliable and simple when applied to macrosamples, but for small quantities it fails because the ethyl acetate cannot be completely hydrolyzed without employing a standard alkali solution too strong to yield accurate results. Both general procedures also suffer from the fact that they are too time-consuming, or the apparatus or manipulative details required are too complicated, or both.

A semi-microprocedure for the determination of acetyl, especially in O-acetyl compounds, based upon a different principle and largely free from the disadvantages enumerated, is presented for consideration. With few exceptions it has given uniformly good results with all compounds upon which it has been tried, and its accuracy is also well within the range for which it is intended. The method involves (1) the hydrolysis of the acetyl compound with *N* ethanolic potassium hydroxide; (2) the dilution of the reaction mixture to a definite volume with strong magnesium sulfate solution acidified with sulfuric acid; (3) the distillation of the liberated acetic acid at constant volume; and (4) the titration of the first 50 cc. of the distillate with 0.02 *N* alkali.

Under the conditions of the experiment and within the concentration range intended, the total quantity of acetic acid is calculated from the distillation constant of acetic acid. For

the purpose at hand this constant is defined as that percentage of the total acetic acid present in the distilling flask which comes over in the first 50 cc. of distillate. With the apparatus shown in Figure 1 and the reagents indicated below this value is 95.7.

A 10- to 20-mg. sample of the material to be analyzed is weighed upon a 12 × 24 mm. piece of cigaret paper and placed, with the paper, in the distilling flask, *B*. Two cubic centimeters of *N* ethanolic potassium hydroxide are then added, and the liquid is heated to boiling or until all the sample is dissolved. After 4 minutes 18 cc. of magnesium sulfate-sulfuric acid solution, made by dissolving 100 grams of crystalline salt and 1.5 grams of concentrated sulfuric acid in sufficient water to make 180 cc., are added. Steam, generated in flask *A*, is then passed through the apparatus, and flask *B* is heated with a small flame in such a manner that the liquid in the flask distills at a fairly rapid rate and at a constant volume. Fifty cubic centimeters of the distillate are collected and titrated to a permanent pink color with 0.02 *N* potassium hydroxide, phenol red being used as an indicator. The acid obtained represents 95.7 per cent of the total acetic acid formed from the hydrolysis of the acetyl compound from which the percentage of acetyl in the sample is calculated.

Table I gives some results obtained by the method.

TABLE I. ANALYSIS OF SEVERAL ACETYL COMPOUNDS

Substance	Sample Mg.	Acetyl Found %	Acetyl Calcd. %	Deviation from Theory %
Cellobiose octaacetate	10.14 11.74	51.1 50.5	50.7 ..	+0.6 -0.2
Diacetyltoxicarol	23.51 22.20	17.1 17.0	17.4 ..	-0.3 -0.4
Monoacetyldihydro- desoxytoxicarol	21.70	9.7	9.8	-0.1
β -Naphthol acetate	22.50	22.8	23.1	-0.3
Acetylmethyl ursolate	23.25	8.5	8.4	+0.1
S-Acetyl-1-thioben- zoxazole	21.53	22.4	22.3	+0.1
Pentacetylquercetin	9.92	42.4	42.0	+0.4
Acetylhelanalin ^a	24.09	13.4	14.1	-0.7
Hexacetylalogossypol ^b	20.31	34.7	36.1	-1.4
	17.00	34.6	..	-1.5
Acetylsalicylic acid	13.88	30.0	23.9	+6.1
	18.41	29.3	..	+5.4
Acetanilide	14.72	31.9	31.9	0.0
	14.38	31.8	..	-0.1
Acetyl <i>m</i> -toluidine	14.22	29.0	28.8	+0.2
<i>n</i> -Acetylthiodiphenyl- amine	21.85	18.1	17.8	+0.3
Acetyldiphenylamine	14.40	21.0	20.4	+0.6

^a Perkin's O-acetyl method (3) gave 9.6 per cent.

^b Perkin's O-acetyl method gave 25.5 per cent acetyl; his N-acetyl method gave 34.5 per cent acetyl (1).

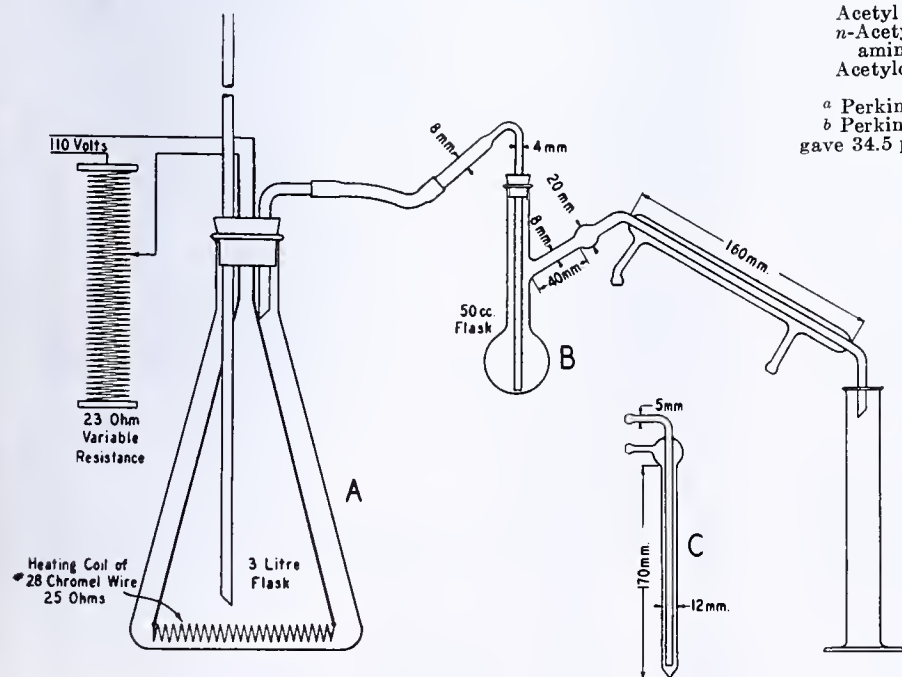


FIGURE 1. DIAGRAM OF APPARATUS

By modifying the above procedure it may be applied to many N-acetyl compounds. A few such materials have been analyzed by the following modification: The sample, placed in the distilling flask, is dissolved in 2 cc. of *N n*-butanolic potassium hydroxide solution. The condenser, *C*, is placed in the flask, and the mixture is refluxed for 1 hour. The procedure is then the same as for O-acetyl compounds, except that a blank must be run upon the reagents and the resulting correction applied to the titration. A distillation constant of 96 should be used. Some results obtained in this way are included in Table I.

It is recommended that the distillation constant for pure acetic acid be determined for each apparatus, as relatively small changes in the size and shape of the distilling flask caused

some differences in these values, and that the 0.02 *N* potassium hydroxide be frequently checked against a standard acetic acid.

As previously indicated, the method, with few exceptions, has given uniformly good results with all compounds upon which it has been tried. These exceptions, however, indicate its limitations, for unsatisfactory results are obtained with substances that react with alkali to give products which upon acidification are volatile with steam and will affect the titration. The results with acetylsalicylic acid presented in Table I are included to illustrate this point. Under the conditions of the experiment salicylic acid is somewhat volatile, and that which passes over is titrated with the acetic acid. This difficulty, however, could be overcome in many cases by running a blank upon the unacetylated mother substance and deducting the results from the values obtained upon the acetyl de-

rivative. It is also possible that O-acetyl compounds may be encountered which react slowly because of their insolubility, but which would react upon longer boiling. In such cases correct results should be obtained by running a blank upon the reagents under the conditions of the experiment and if necessary applying the above suggestion. Notwithstanding these limitations, which are not of frequent occurrence, the method is believed to be a valuable analytical tool.

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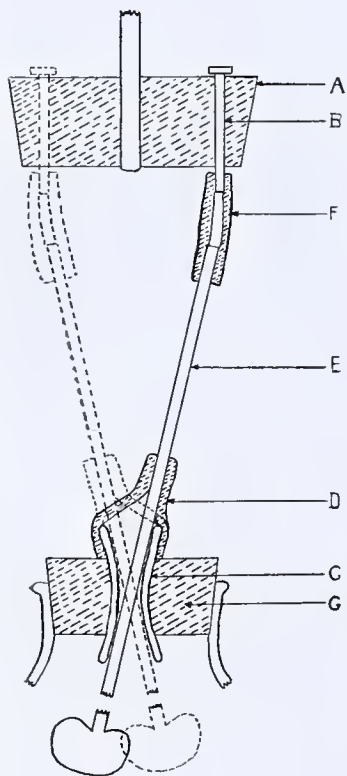
A New Sealed Stirrer for the Laboratory

LEO S. POWELL, Rutgers University, New Brunswick, N. J.

A NEW sealed stirrer has been developed which eliminates the use of a mercury seal. This stirrer has been used by the author and found to be completely satisfactory for the preparation and reaction of Grignard reagents. The materials needed are easily obtainable in any chemical laboratory and the whole stirrer can be made and assembled in one hour.

The eccentric drive, *A*, is made from an ordinary No. 12 solid rubber stopper by drilling a hole through the center for the motor shaft. Another hole at about 2.5 cm. from the center acts as a bearing for the glass shaft, *B*, which is made from a 6-cm.

piece of ordinary soft-glass rod of 4-mm. diameter, by heating one end and pressing it against a piece of asbestos board so as to produce a flange on the end which prevents it from falling through *A*. Shaft *B* should fit loosely enough into *A* so that it can rotate freely and may be lubricated with a drop of paraffin oil. Part *C* is made from a piece of glass tubing of 11-mm. diameter and 6-cm. length, and is flanged at both ends in the manner shown. By placing stirrer *E* inside of *C* and rotating it by hand, one can determine to what extent tube *C* must be flanged. *D* is a piece of soft-rubber tubing fitted over *C*, forming the seal between *E* and *C*. *F* is a short piece of rubber tubing connecting the eccentric drive, *B*, to the stirring rod, *E*. In setting up the stirrer it is essential to place a good clamp around the upper part of *C*. This diminishes vibration and also prevents the stopper, *G*, from working loose. The dimensions given are by no means rigid and may be varied to suit the conditions.



The advantages that this stirrer offers over the ordinary mercury-sealed stirrer are: (1) It produces agitation which is as efficient, if not more so, than that produced by the mercury-sealed stirrer. (2) The same stirrer may be made to fit any size flask by simply changing the size of stopper *G* and adjusting the position of rod *E*. (3) It is simple and easy to make and eliminates the use of mercury.

RECEIVED August 10, 1936.

Automatic Leveling Device for Gas Collection by Downward Displacement of Mercury

LYNN D. WILSON

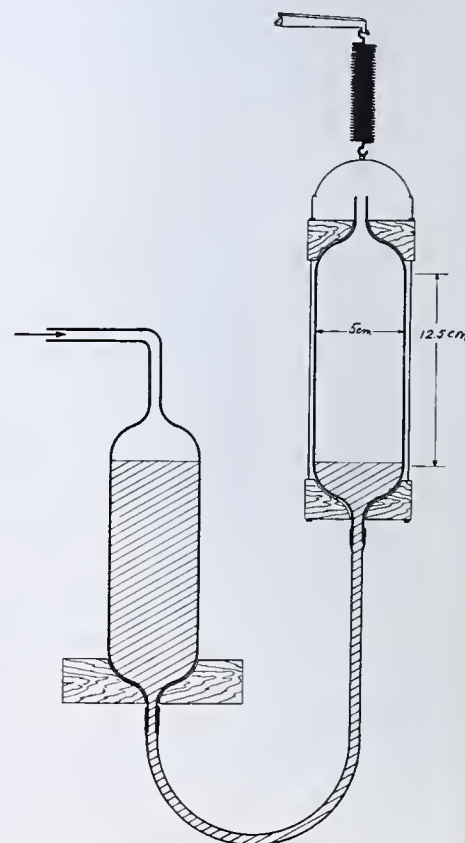
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IN THE collection of gases by downward displacement of mercury, manual control of the leveling flask is precluded when the gas evolution is very slow. The difficulty is readily removed by means of an automatic spring control as shown in the accompanying figure.

The Pyrex collecting and leveling flasks are of the same dimensions and are mounted on felt-covered wooden supports. Heavy wire connects the blocks holding the leveling flask. The spring is suspended from a rod clamped to a ringstand, so that the starting levels may be adjusted.

Analysis of the dynamics of this arrangement shows that flasks of constant cross-sectional area must be used; hence the starting levels must be adjusted to a position where further change in level will not be accompanied by a change in cross section.

If the force constant of the spring is suitable and the rubber tubing connecting the flasks is sufficiently flexible, the gases may be collected at atmospheric pressure to within 1 to 2 mm. The apparatus may be used for other pressures by applying suction or pressure to the leveling flask.



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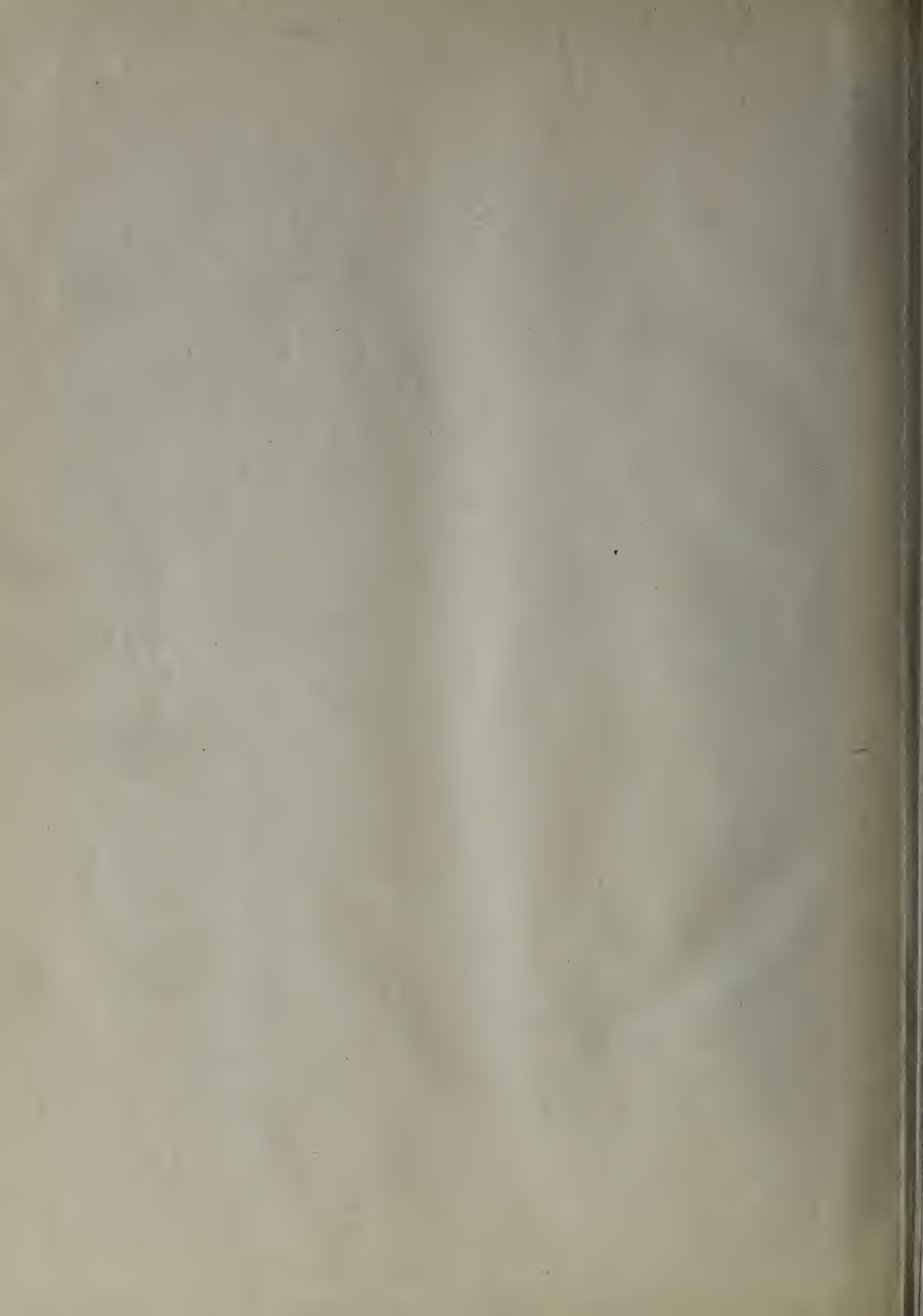
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